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ELECTROCHEMICAL PREPARATION OF COPPER-NICKEL AND COPPER-NICKEL- MANGANESE ALLOYS AND CHARACTERIZATION

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ABSTRACT

Electrochemical preparation of binary alloy of Cu-Ni from acid sulphate bath containing citric acid using potentiostatic method. The effects of alloy composition were monitored. Copper is widely used in industry, because of its good thermal conductivity and mechanical properties. The addition of Nickel and Manganese to Copper improves its strength and durability and also the resistance to corrosion and erosion. Corrosion controls of metal have technical environmental and economical importance. The Cu-Ni-Mn alloy used commercially for decorative and protective purpose and also in marine applications. The thin film coating characterized by SEM, EDAX and XRD shows morphological, compositional and structural properties of alloys respectively.

KEYWORDS :*Electrochemical preparation , Copper-Nickel and Copper-Nickel- Manganese , characterization.*

1.INTRODUCTION :

Copper has excellent corrosion resistance in the environment and fresh water. In sea water, the Cu-Ni alloys have superior resistance to corrosion. Copper is the most noble metal in common use. The addition of Nickel to Copper improves its resistance to corrosion and erosion. After including Mn in Cu-Ni alloys shows the excellent resistance to marine corrosion as well as stress corrosion cracking. Cu-Ni-Mn alloys have advantage to high resistance and application to marine chemical environment for ship, boat hulls and heat exchange equipment[1-4]. Cu-Ni-Mn alloys posses excellent thermal and electrical properties[5-6]. Owing to their outstanding properties, pure Copper and Copper-rich alloys are being extensively used in a wide range of technological and metallurgical applications. For example, the combination of high electrical and thermal conductivities has prompted the utilization of these materials in microelectronic devices and integrated circuits, better ductility than many other metals, which is advantageous in terms of mechanical workability and permits the manufacture of micro wires and a variety of devices with small lateral sizes. However, a large hardness may be desirable in certain applications, for example when Cu has to be subject to high tension in a welding. In principle, one can increase Cu strength by reducing the grain size (i.e., work hardening) or by alloying it with another metal.[7-10]. Cu-Ni 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 and almost the same lattice parameters. Cu-Ni alloys found applications such as corrosion resistance and decoration in industrial area [11-12]. To achive the co-deposition of copper and nickel, the addition of Complexing agents are necessary to diminish the gap between the reduction potential of Cu(II) and Nickel(II) species, trisodium citrate and ammonia seem to be among the most efficient compound [13-15] . The objective of present study of Cu-Ni and Cu-Ni-Mn coating is reduced the Corrosion rate and study the morphology, % composition and structure of Cu-Ni and Cu-Ni-Mn coating.

2. EXPERIMENTAL DETAILS

Material $\rightarrow$ Analytical grade chemicals of $CuSO_4.5H_2o$, $NiSO_4.XH_2o$, $MnSO_4.H_2o$, H_3Bo_3 (Boric acid),C6H8O7 (Citric acid), HCl, H_2SO_4, NaCl and distill water. Three electrode assembly, digital-millimeter, power supply, voltage stabilizer, calomel electrode used as reference, 1cm2 mild steel plate used as working as well as counter electrode.

Method$\rightarrow$Electrochemical preparation is carried out by potentiostatically using sulphat bath with three electrode configuration. Current efficiency and potential measured by multi-meter. Co-deposition potential of Cu-Ni is found out by Current/Potential data. pH of the solution is maintain as acidic. HCl, H_2SO_4, and NaCl used as corroding solution and corrosion rate calculated by tafel plot (polarization curve). Using following equation.

CR = Icorr x 0.13x Eq.Wt./ F x d x A
Where,
CR = Corrosion Rate
Eq.Wt. = Equivalent weight of Cu-Ni and Cu-Ni-Mn
F = Faraday's constant
D = Density of Cu-Ni and Cu-Ni-Mn
A = Area of the substrate

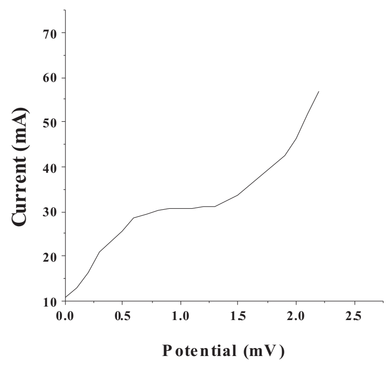
Current voltage behavior of the materials is studied to construct tafel plots and polarization studies.HCl, H_2SO_4, NaCl used for testing of deposited Cu-Ni and Cu-Ni-Mn alloys. Corrosion rate were determined by tafel plot. Current efficiency and potential measured by digital-multimeter, Surface morphology, Composition, Crystal structure determined by SEM, EDXA & XRD respectively.

3. RESULT AND DISCUSSION

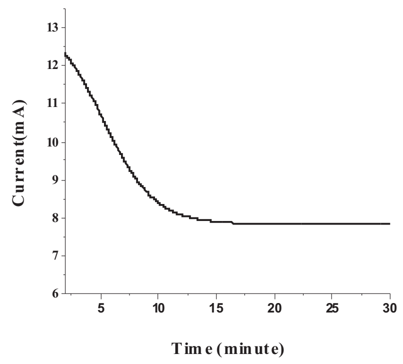
Preparation of Cu-Ni binary alloy and make than more better after addition of third element Mn. Electrodeposition of binary ternary alloy of Cu-Ni, Cu-Ni-Mn respectively. Deposition potential of binary, ternary alloys measured by with the help of Current-Voltage data (Fig-1). Co-deposition potential of coating Cu-Ni & Cu-Ni-Mn alloy was carried out at -0.4 mV Vs SCE electrode. Dipped stainless steel electrodes in electrolytic solution at least in 5-8 minute to established the equilibrium then apply the Co-deposition potential -0.4 mV. In starting of deposition current lower the fastly up to steady state value. During the 30 minute deposition of Cu-Ni & Cu-Ni-Mn alloys current value noted with the equal interval of time and then plotted the graph (Fig-2). Current–time graph gives the information about thickness of thin films. The data shows that the higher amount of Mn gives more thick film of Cu-Ni-Mn. During the deposition of alloys, concentration of Cu-Ni kept constant and varies the concentration of Mn.

In this experiment Boric acid and Citric acid are used to improve the deposited properties of Cu-Ni-Mn alloys. Boric acid maintain the pH of the solution and used as catalyst to improve the quality of deposited material Cu-Ni-Mn and it also affect the compositional and morphological properties of Cu-Ni-Mn ternary alloy. Citric acid used as complexing agent it closer the deposition potential of Cu-Ni, Cu-Ni-Mn alloy.

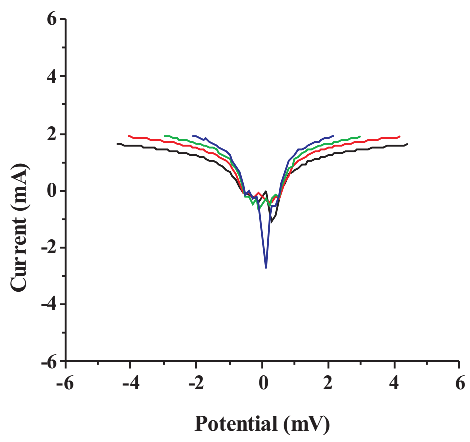
After 30 minute deposition, the deposited Cu-Ni, Cu-Ni-Mn alloys were tested in various type of corroding solution of H_2SO_4, HCl, and NaCl having different concentration. The polarization studies have been made by cathodic and anodic polarization. Tafel plot construct with the help of cathodic and anodic data (Fig-3). The potential of working electrode was varied with respect to corresponding current flowing between the working to counter electrode. Corrosion properties of Cu-Ni, Cu-Ni-Mn alloys at various concentration shows, the low concentration of Mn is good for Cu-Ni-Mn alloys. Corrosion rate decreases with decreases the amount of Mn in electroplating solution. Cu-Ni has better corrosion resistance than Copper, Cu-Ni alloy with addition of Mn have more corrosion resistance than Cu-Ni alloys.



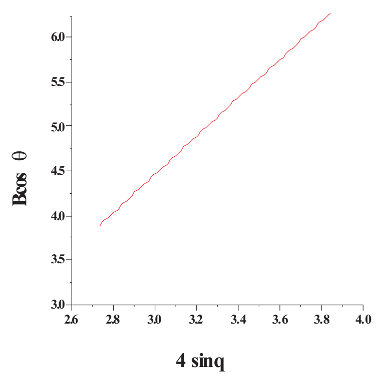
potential-Current graph for find
Co-deposition potential-(Fig-1)



Current Vs Time graph for calculating thinfilm of alloy(Fig-2)



Cu- Ni Tafel plot(Fig-3)



Williamson-Hall plot
(Fig-7)

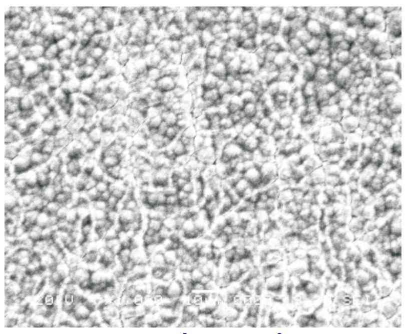
Corrosion rate for Cu Ni coating in different corrosion medium 10-4 mpy
Corrosion rate

Corrosion medium H2so4	0.1M Cu ,0.1M Ni	0.1Cu, 0.1Ni, 0.01Mn	0.1Cu, 0.1Ni, 0.02Mn	0.1Cu ,0.1Ni ,0.03Mn
0.01N	0.154	0.0412	.0341	.0136
0.02N	0.192	0.0108	.0397	.0454
0.03N	0.211	0.0511	.0735	.0625
0.04N	0.267	0.0341	.1477	.2499

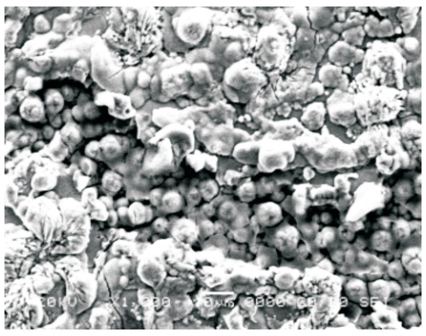
Corrosion medium Hcl	0.1M Cu,0.1M Ni	0.1Cu ,0.1Ni ,0.01Mn	0.1Cu,0.1Ni , 0.02Mn	0.1Cu,0.1Ni, 0.03Mn
0.01N	0.1540	0.0198	.0397	.0568
0.02N	0.1880	0.0136	.0341	.0540
0.03N	0.2130	0.0682	.1079	.1193
0.04N	0.0234	0.0625	.1136	.1136

Corrosion medium NaCl	0.1M Cu, 0.1M Ni	0.1Cu ,0.1Ni ,0.01Mn	0.1Cu,0.1Ni ,0.02Mn	0.1Cu,0.1Ni ,0.03Mn
0.1%	0.1060	0.0125	.0341	.0477
0.2%	0.1540	0.0795	.0414	.0568
0.3%	0.2130	0.0170	.1193	.0909
0.4%	0.2340	0.0738	.1682	.1227

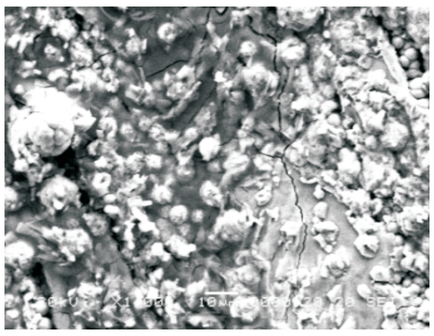
SEM image of Cu-Ni alloys in equal amount of Cu-Ni shows regular and shape size of the grain. The average size of the deposits was 10 µm Fig-4(a). The morphology and surface area of Cu-Ni alloys having 0.02M Mn concentration shows the large grain size of the particle having unequal size. The minimum size of the particle is 10µm they look like the Cauliflower Fig-4(b). In 0.03M concentration of Mn contain with Cu-Ni deposits show the unequal size of large particle like Cauliflower Fig-4(c). EDAX analysis of Cu-Ni & Cu-Ni-Mn alloys shows the atomic percentage of deposited element and also give the information about elements present in alloy Fig-5-a,b,c). XRD data shows the structural features of deposited alloys. XRD of electrodeposited Cu-Ni and Cu-Ni-Mn thin film structure shown in (Fig-6-a,b,c,d). The peak obtained from XRD of Cu-Ni and Cu-Ni-Mn thin film compared with the reference pattern of JCPDS card standard peak. Sample was indexing successfully, to determine the crystal structure and particle size. Crystal structure Cu-Ni and Cu-Ni-Mn thin film found to be FCC (Face centered cubic). Particle size calculated from Scherer equation, which found to be lesser than 100nm. The micro strain induced on surface of thin film can be attributed to crystal imperfection and distortion. A representative Williamson's Hall plot is shown in (Fig-7). The growth of internal stresses in the electrodeposited thin film is determined by it. In some samples the slopes were found be negative indicating compressive stress while in some cases it was positive indicating tensile stress.



(Fig-4,a)

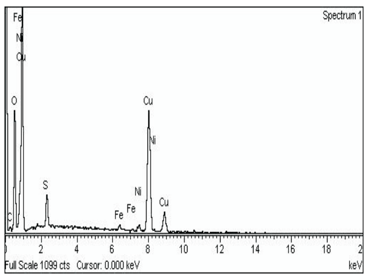


(Fig-4,b)

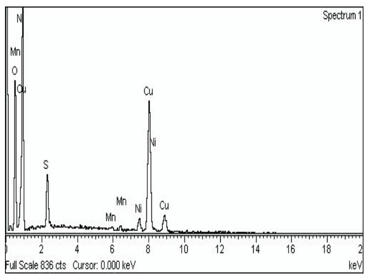


(Fig-4,c)

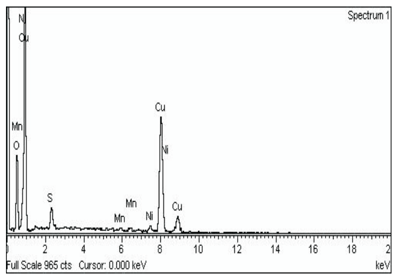
(Fig-4,a).SEM of .01MCu-0.1M Ni alloy
(Fig-4,b).SEM of .01M Cu-0.1M Ni-0.02M Mn
(Fig-4,c).SEM of .01M Cu-0.1M Ni-0.03M Mn



(Fig-5,a)

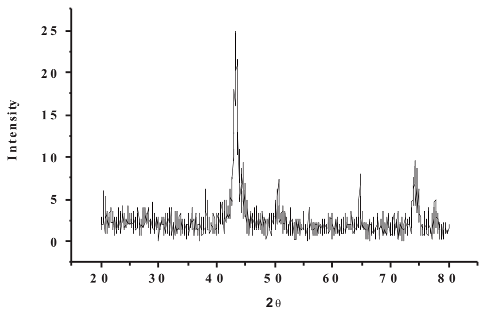


(Fig-5,b)

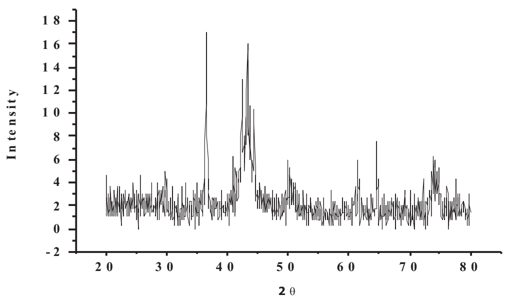


(Fig-5,c)

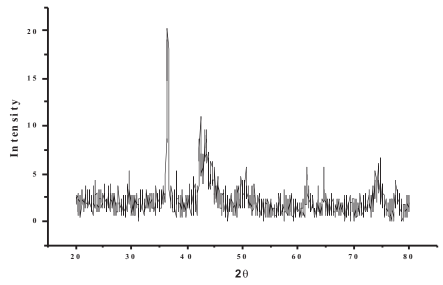
(Fig-5,a).EDAX of 0.1M Cu-0.1M Ni alloy
(Fig-5,b).EDAX of 0.1M Cu-0.1M 0.02M NiMn alloy
(Fig-5,c).EDAX of 0.1M Cu-0.1M Ni-0.03M Mn alloy

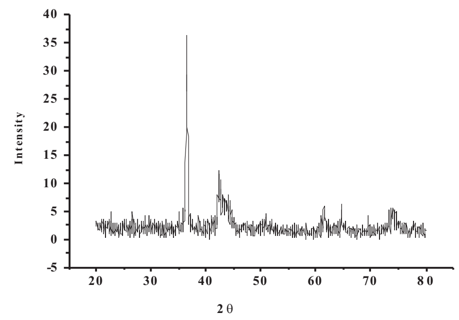


XRD of .01MCu-0.1M Ni alloy(Fig-6,a)



XRD of .01MCu-0.1M Ni-0.01M Mnalloy(Fig-6,b)





XRD of .01MCu-0.1M Ni-0.02M Mn alloy(Fig-6,c) XRD of .01MCu-0.1M Ni-0.03M Mn alloy(Fig-6,d)

CONCLUSION

Cu-Ni alloys have better corrosion resistance than Cu, Cu-Ni alloys with addition of Mn have more corrosion resistance than Cu-Ni binary alloy. Low concentration of Mn is good for Cu-Ni-Mn ternary alloys. With increasing concentration of Mn in electrolytic solution, Corrosion rate also increases. EDAX shows, presence and percentage of Cu-Ni binary and Cu-Ni-Mn ternary alloys. SEM image of binary and ternary alloy shows the morphological features. XRD shows the crystal structure Cu-Ni binary and Cu-Ni-Mn ternary alloys. Boric acid and citric acid also play significant role in Cu-Ni-Mn alloys. It act as complexing agent and closer the deposition potential of Cu-Ni-Mn alloys.

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