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Comparative study of electrowinning of copper and cadmium in presence of some new additives.

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Abstract-Inhibition behavior of some new additives such as diethyl ether was investigated by cathodic polarization in order to generate the quality of the cathodic copper, the result indicate that inhibition performance of these additive are depend on complex and adsorption behavior as well as deposited potential. The effect of additive on current efficiency, morphology, stability and particle size was studied by SEM, and Avrami- Erofeev kinetics. The current efficiency was found to decrease from 62.13% to 38.9% with increase in concentration of additive.The stability of cadmium decrease from 68.28% to 25.44% with increase in concentration of additives. The deposited were dendrite acicular polygonal and their average particle size decrease with increase in concentration of additive.

Keyword - Electrowinning, morphology, additives, Avrami- Erofeev kinetics.

Introduction

Powder metallurgy has the distinction of being at the same time one of the oldest and one of the most modern methods known for the fabrication of metal articles. A powder can be precipitated at the cathode of an electrolytic cell under certain operating conditions. The main benefit of an electrolytic method is its high product purity. A number of patents have been taken on the powder fabrication since early decades of twentieth century. Osborn et al [1] and Smith [2-5] studied the electrolytic preparation of copper powder Dutra et al [6-8] studied the electrorefining in flow by cell for cadmium removal from dilute aqueous solutions, Elsherief [9] studied the efficient cadmium removal from acidic solution by using a flow cell with spiral wound steel electrode. In our previous [10] electrolytic conditions for the powdered deposition of copper were determined and effect of diethyl ether was studied.

In this paper, an attempt has been made to study comparatively the optimized parameters for potentiostatic deposition of metals like copper, cadmium as powder. At optimized conditions the influence of diethyl ether is studied with reference to current efficiency and kinetic aspect. The comparative study of particle size in presence of non-polar additive is presented.

Experimental

All the chemical used for the experiment were of analytical grade(A.R.)and double distilled water was used for preparing the required bath solutions. Bath solution consist of the sulphate salts of metals copper , cadmium . Bath solutions for copper and cadmium were prepared in acidic medium. Sulphuric acid was used as a solvent for copper and cadmium. Electrowinning was carried out in a two electrode electrochemical cell with graphite electrode (2.5 cm x 2.5 cm x 9 cm) as the anode and stainless steel electrode (1.5 cm x 9 cm x 1.5 mm) as cathode. Constant potential was supplied by using the potentiostat (Model 1399) fabricated by CECRI, Karaikudi, India (CSIR Lab.)

The experiment was carried out in two parts. In the first part optimized electrolytic parameters (salt concentration, solvent concentration and potential applied) were determined for the powdered deposition of metals. In the second part the effect of diethyl ether was studied by varying the concentration of diethyl ether in the optimized bath condition. The powdered deposit was scraped with the force of water, washed and dried over vacuum oven at 95 ^{0}C and analyzed its particle size. During the electrowinning the kinetics of the deposition of metal powder was studied by withdrawing 10 ml of bath solution at regular interval and titrated against EDTA using fast sulphon black F indicator. The electrowinning was carried out for two to three hours. The metal powder was analysed for particle size at STIC Cochin University, Kochi.

Results and Discussion

Deposition of copper

$$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$$

$$2H^+ + O^{2-} \longrightarrow H_2O$$

$$SO_4^{2-} + H^+ \longrightarrow HSO_4^-$$

$$H_2SO_4 \longrightarrow HSO_4^- + H^+$$

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At Anode

$O^{2-} \longrightarrow O + 2e$

$O + O \longrightarrow O_2$

At Cathode

$Cu^{2+} + 2e \longrightarrow Cu$

Deposition of cadmium

$CdSO_4 \longrightarrow Cd^{2+} + SO_4^{2-g}$

$H_2O \longrightarrow 2H+ + O^{2-}$

$SO_4^{2-} + H^+ \longrightarrow HSO_4^-$

$HSO_4^- + H+ \longrightarrow H_2SO_4$

At Anode

$O^{2-} \longrightarrow O + 2e$

$O + O \longrightarrow O_2$

At Cathode

$Cd^{2+} + 2e \longrightarrow Cd$

The cathodic current efficiency decreases as the concentration of diethyl ether in the bath solutions increases. The additive causes the hindrance to the cations mobility towards cathode. As a result deposition rate decreases which ultimately causes the lower C. E. It is also found that the C. E. decreases linearly with increases in addetive concentration. But this we cannot say for every metal.

Kinetic study

During the electrowinning the kinetics of electrodeposition of metals was studied in presence of additive diethyl ether. The plot of –log α against time gave a straight line (eq 1). /fig. (1)

$-\log \alpha = mt + c$ …….. (1)

Where $\alpha = (Ci-Ct/Ci)$,

Ci and Ct are the initial and final concentration of the metal in the bath solution. It is found that the slope of the graph decreases as the concentration of diethyl ether in the bath solution increases. Additive causes the hindrance to the metal ions to move freely towards the cathode which results in the decrease in the rate of deposition of metal powder.

Table1. Relative parameters and their conditions applied for copper and cadmium

Parameter	Optimized condition
$CuSO_4.5H_2O$	35.97 g/l
H_2SO_4+ diethyl ether	0.5N+5% to 30%
Bath voltage	4.0 V
Bath Temp.	30±1^{0}C

Parameter	Optimized condition
$3CdSO_4.8H_2O$	5.25 g/l
H_2SO_4+ diethyl ether	2N+5% to 30%
Bath voltage	4.0 V
Bath Temp.	30±1^{0}C

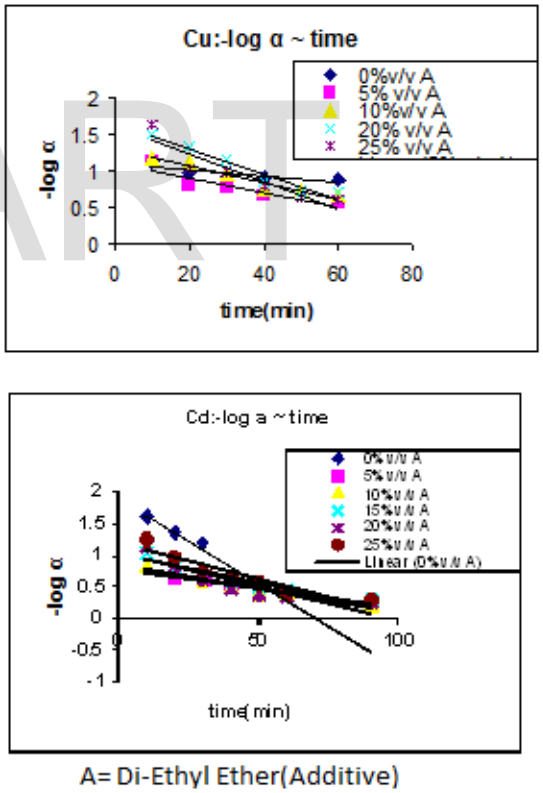

Fig. (1) graph representing decrease in conc. of Et-o-Et.

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Table 2.Morphology of copper powder and related data Concentration

Concentration H2SO4 (N)+ Diethyl ether (%)	Apparent Density (gm/ml	Current Efficiency (%)	Stability of powder (%)	Range of particle size (nm)	Morphology of electrodeposited powder
0N+5%	7	62	81.4	208-482	Hexagonal, dendrite,
0N+10%	5.7	42.62	70.7	247-434	Hexagonal, dendrite, sponge,
1N+10%	2	40	68.7	203-475	Hexagonal, sponge, acicular,
1N+15%	2.1	38.9	62.35	247-456	Hexagonal, acicular, sponge.

Table3.Morphology of Cadmium powder and related data Concentration

Concentration H2SO4 (N)+ Diethyl ether (%)	Apparent Density (gm/ml	Current Efficiency (%)	Stability of powder (%)	Range of particle size (nm)	Morphology of electrodeposited powder
0N+5%	2.05	21.42	68.28	12.52-38.48	Polygonal with flaky layers,
0N+10%	19.16	31.48	59.93	62.54	Polygonal with flaky layers, underdeveloped dendrite,
1N+10%	6.21	25.41	52.65	118.28	Flaky acicular with cubical built.
1N+15%	19.34	33.03	25.44	263.81	Semi developed dentrites,flaky polygonal

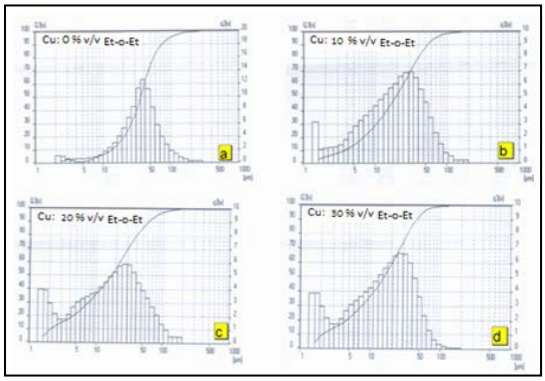

Fig. (2) Variation in partical size of Cu, at diff.conc.

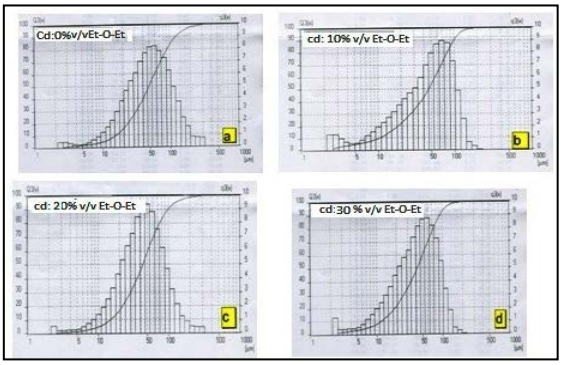

Fig. (3)) Variation in partical size of Cd, at diff.conc.

Conclusion

In 1.0 N sulphuric acid and 15% diethyl ether medium more than 60 to 65% particles are below 247nm and nano-particles are in the range of 247-456nm. SEM micrograph of cadmium powder and revalent data represent that lower the apperent density smaller is the partical sizeof electrodeposited powder

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