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A VOLTAMMETRIC STUDY ON THE ELECTRODEPOSITION AND DISSOLUTION OF CADMIUM IN PLATING SOLUTIONS

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Cadmium is electroplated for a wide variety of applications especially in the aerospace and defence field. This paper deals with a voltammetric investigation on some of the electroplating solutions of cadmium like sulphate, sulphamate and cyanide. From the results electrodeposition and dissolution characteristics of cadmium are suitably explained.

Keywords: Cadmium, electrodeposition and dissolution, sulphate, sulphamate, cyanide and voltammetry

INTRODUCTION

Cadmium is electroplated for a variety of industrial applications - for fasteners, electric relays, marine hardware, electrical engine bushings and bearings, automotive parts, aircraft and defence components etc. [1-2]. These applications take advantage of the very desirable properties of cadmium namely, good sacrificial corrosion protection, lubricity, solderability, low electrical contact resistance, tendency to form only low volume corrosion products. Aerospace and defence industries are the major specifiers of electrodeposited cadmium.

Electrodeposition of cadmium from various types of electrolytes like sulphate, chloride, sulphamate, fluoborate and cyanide are reported in literature [2-9]. The present paper deals with a cyclic voltammetric investigation of the electrodeposition and dissolution of cadmium from solutions based on sulphate, sulphamate and cyanide.

EXPERIMENTAL

Solutions for this investigation were prepared using AR chemicals and double distilled water. Cadmium as sulphamate and cyanide were prepared starting from cadmium sulphate, by precipitating cadmium as hydroxide, filtering and washing it, followed by dissolving it in calculated amount of sulphamic acid and potassium cyanide respectively. Cadmium content in the solution was kept at 0.5 *M*, a concentration of the same order as that in normal plating electrolytes so that the behaviour of electroplating solutions can be compared.

The cell used was an all glass two compartment cell. Glassy carbon or cadmium, platinum and saturated calomel electrodes were used as working, counter and reference electrodes respectively. The working electrode was prepared by embedding in teflon sheaths 0.5 cm thick discs of electrode materials cut off from rods so that a specific geometric area is exposed at the operative end of the electrode. The areas of glassy carbon and cadmium electrodes used were 0.25 and 0.17 cm^2 respectively. The working electrode was polished with emery paper - 1/0 to 4/0 grade, degreased with trichloroethylene, washed thoroughly and rinsed before introduction into the experimental solutions.

The cell was connected to a potentiogalvanoscan (PGS 81, Wenking) for applying the potential sweep required. The resulting current voltage

response was recorded with an X-Y recorder (Rikadenki, RY - 101A).

RESULTS AND DISCUSSION

Cadmium sulphate, sulphamate and cyanide solutions were subjected to voltammetric investigations by applying a triangular potential sweep. During the cathodic potential sweep, there was no significant current flow upto a potential (E_d) corresponding to the decomposition potential of that electrolyte; current rises gradually at more cathodic potentials and in many cases this is immediately followed by another steeper rise suggesting the onset of hydrogen evolution. The presence of ammonium sulphate or sulphamate was found to be favourable in making the deposition peak steeper and separating it from hydrogen evolution peak. The nature of the anodic part of the cyclic voltammogram, which manifests the dissolution of the deposited metal, depends on the value of the switching potential (E_λ) in many cases. The anodic peaks were found to be wide in certain cases whereas in other cases they were steep and well defined or split into more than one peak indicating multistep dissolution phenomena. In cyanide solutions, concentration of free cyanide was found to affect the dissolution behaviour. Features observed in individual cases are discussed below.

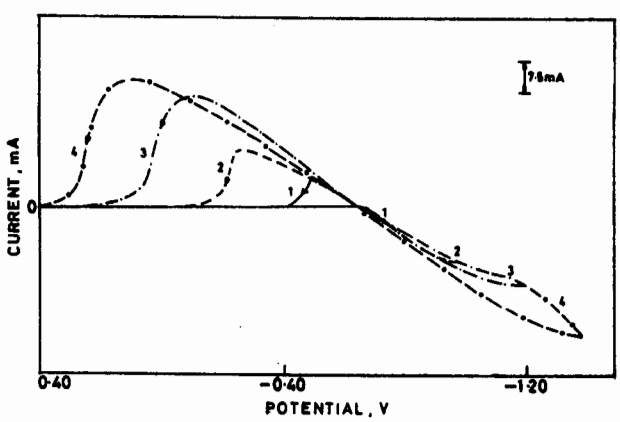

Fig. 1: Voltammograms using glassy carbon working electrode v 0.02 $Vsec^{-1}$ solution 0.5 *M* cadmium sulphate E_λ (1) -0.80 (2) -1.00 (3) -1.20 (4) -1.40 V

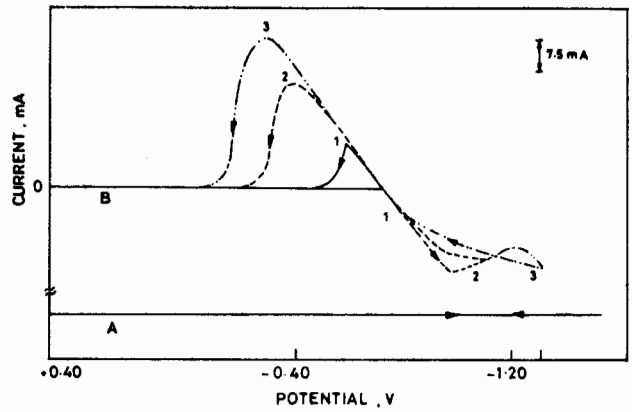

Fig. 2: Voltammograms using glassy carbon working electrode v 0.02 $Vsec^{-1}$ Solution A. 0.5 *M* ammonium sulphate B 0.5 *M* cadmium sulphate + 0.5 M ammonium sulphate E_λ (1) -0.80 (2) -1.00 and (3) -1.20 V

Sulphate solutions

The voltammograms recorded using inert glassy carbon electrode from 0.5 *M* cadmium sulphate solutions are shown in Figs. 1 and 2. Fig. 1 is the voltammogram from 0.5 *M* cadmium sulphate solution. It is seen that deposition of

TABLE I: Cyclic voltammetric parameters for 0.5 *M* cadmium sulphate solutions at 0.02 $Vsec^{-1}$

Concn of ammonium sulphate (*M*)	E_d (V)	$E_{p,c}$ (V)	$I_{p,c}$ ($A.cm^{-2}$)	E_λ (V)	$E_{p,a}$ (V)	$i_{p,a}$ ($A.cm^{-2}$)
0	-0.680	—	—	-0.800	-0.500	0.027
	-0.680	—	—	-1.000	-0.250	0.057
	-0.680	—	—	-1.200	-0.100	0.108
	-0.680	—	—	-1.400	+0.070	0.123
0.20	-0.680	—	—	-0.800	-0.500	0.030
	-0.680	-0.970	0.080	-1.000	-0.340	0.076
	-0.680	-0.970	0.080	-1.200	-0.210	0.120
	-0.680	-0.970	0.080	-1.400	-0.110	0.159
0.50	-0.680	—	—	-0.800	-0.550	0.048
	-0.680	-0.900	0.084	-1.000	-0.370	0.105
	-0.680	-0.900	0.084	-1.200	-0.300	0.150
	-0.680	-0.900	0.084	-1.400	-0.200	0.291

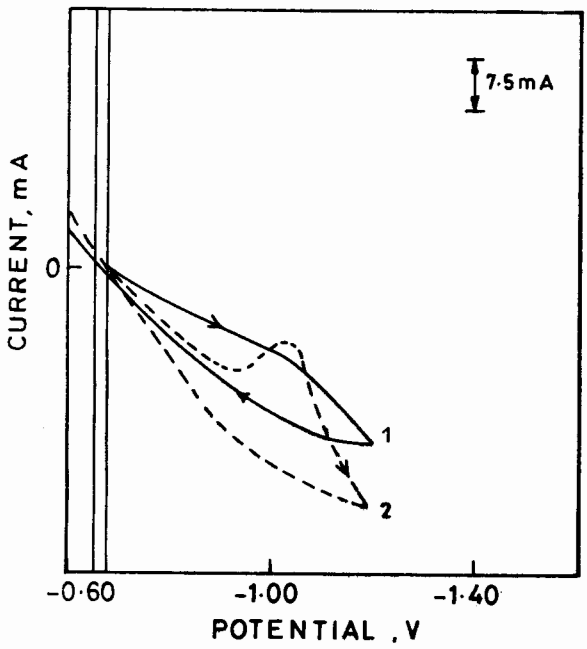

Fig. 3: Voltammograms of cadmium reduction on cadmium electrode v 0.02 $Vsec^{-1}$. Solution 1. 0.5 *M* cadmium sulphate 2. 0.5 *M* cadmium sulphate + 0.5 *M* ammonium sulphate

cadmium starts at -0.680 V, there is a steep increase in current with no characteristic peak indicating hydrogen evolution to occur simultaneously at higher cathode potentials. During the reverse sweep anodic dissolution peak is obtained. When switching potential E_λ is made more cathodic (Fig. 1, curve 1 to 4), there is (Table I) an anodic shift of anodic peak potential $E_{p,a}$ and increase in anodic peak current $I_{p,a}$ corresponding to an increased amount of deposition during the cathodic sweep.

In solutions containing cadmium sulphate and ammonium sulphate, the cathodic voltammogram shows characteristic peak structure (Fig. 2B). Fig. 2A is the background curve in 0.5 *M* ammonium sulphate. Cathodic peak potential $E_{p,c}$ shifts to less cathodic values of ammonium sulphate concentration is increased (Table I and Fig. 2). This shows the favourable effect of ammonium sulphate in facilitating cadmium deposition without hydrogen codeposition. The dissolution peaks are also steeper and occur at less anodic potentials. The increase in peak height indicates the increased amount of cadmium deposited during the cathodic sweep, cathodic shift of $E_{p,a}$ indicates the lowering of dissolution overpotential in presence of ammonium sulphate.

Fig. 3 shows the voltammograms obtained using cadmium working electrode. At potentials cathodic to open circuit potential (OCP) of cadmium,

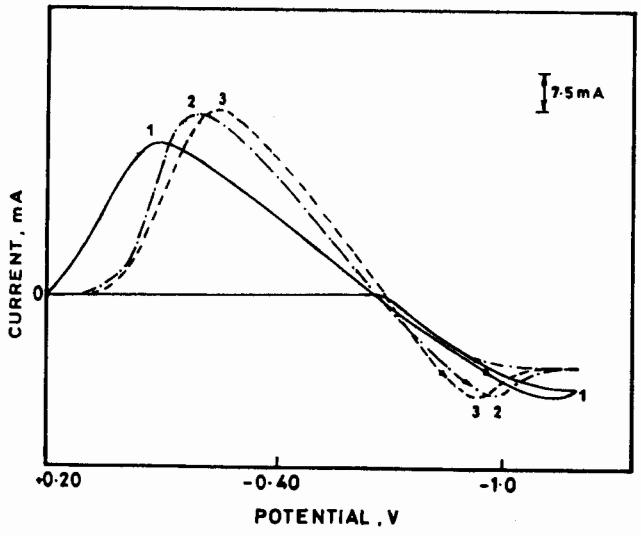

Fig. 4: Voltammetric behaviour of cadmium sulphamate (0.5 *M*) solution on glassy carbon electrode v 0.02 $Vsec^{-1}$ E_λ -1.20 V Ammonium sulphamate concentration (1) 0 (2) 0.40 (3) 0.50 *M*

TABLE II: Cyclic voltammetric parameters for 0.5 *M* cadmium sulphamate solution at 0.02 $Vsec^{-1}$

Concn of ammonium sulphamate (*M*)	E_d (V)	$E_{p,c}$ (V)	$I_{p,c}$ ($A.cm^{-2}$)	E_λ (V)	$E_{p,a}$ (V)	$I_{p,a}$ ($A.cm^{-2}$)
0	-0.680	—	—	-0.800	-0.490	0.027
	-0.680	—	—	-1.000	-0.280	0.060
	-0.680	-1.100	0.084	-1.200	-0.080	0.120
0.20	-0.680	—	—	-0.800	-0.500	0.042
	-0.680	—	—	-1.000	-0.290	0.072
	-0.680	-1.010	0.084	-1.200	-0.170	0.138
0.40	-0.680	—	—	-0.800	-0.500	0.045
	-0.680	-0.980	0.084	-1.000	-0.330	0.075
	-0.680	-0.980	0.084	-1.200	-0.200	0.141
0.60	-0.680	—	—	-0.800	-0.500	0.057
	-0.680	-0.910	0.084	-1.000	-0.400	0.079
	-0.680	-0.910	0.084	-1.200	-0.260	0.147

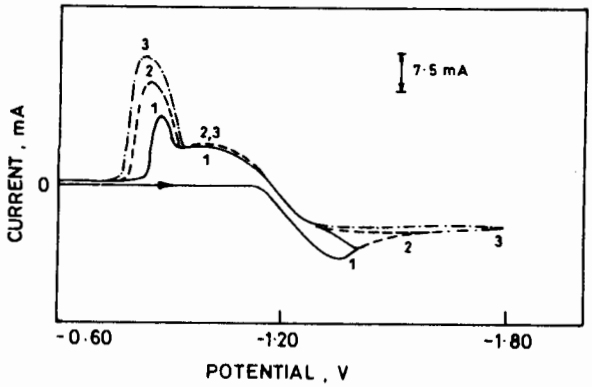

Fig. 5: Voltammograms using glassy carbon working electrode v 0.02 $Vsec^{-1}$ from 0.5 M cadmium as cyanide complex. E_λ (1) -1.40 (2) -1.60 (3) -1.80 V

deposition occurs which changes over to hydrogen evolution at more cathodic potentials (curve 1). Steeper cathodic curve with well defined cathodic peak is observed in solutions containing ammonium sulphate also (curve 2). Anodic sweeping beyond OCP in these cases resulted in a steep increase in current because this will lead to dissolution of silver from the electrode also along with the deposited cadmium.

Sulphamate solutions

Cyclic voltammogram recorded using glassy carbon working electrode from 0.5 *M* cadmium sulphamate solutions are shown in Fig. 4. E_d, $E_{p,c,}$, $I_{p,c,}$, $E_{p,a,}$ and $I_{p,a}$ are listed in Table II. E_d of -0.680 V is identical with that for cadmium sulphate solutions but the cathodic currents are slightly higher and the cathodic and anodic peaks are well defined. From solutions containing ammonium sulphamate also, deposition as well as dissolution peaks become sharper, similar to the results observed with ammonium sulphate addition to cadmium sulphate solutions.

Voltammograms recorded using cadmium working electrode also showed similar trends.

Cyanide solutions

In cadmium cyanide solutions with calculated amounts of cyanide for complexing only, but no free cyanide, deposition starts at - 1.150 V (Fig. 5)

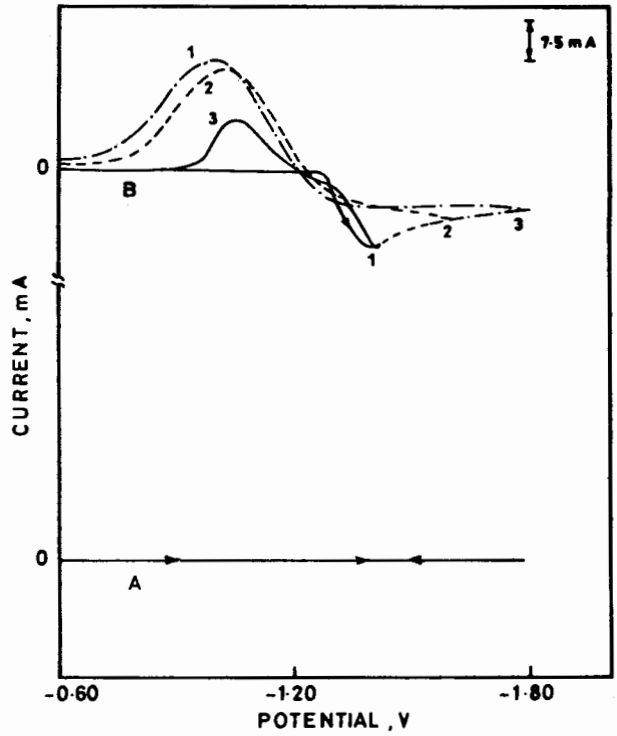

Fig. 6: Voltammograms using glassy carbon electorde at 0.02 $Vsec^{-1}$ solution A 1 *M* KCN alone B 0.5 *M* cadmium as cyanide + 1 M KCN E_λ (1) -1.40 (2) -1.60 (3) -1.80 V

compared to -0.680 V for cadmium sulphate or sulphamate (Figs. 1-4). This can be explained to be due to the complexing effect of cyanide which increases the overpotential for cadmium reduction. Well defined cathodic peaks are obtained and anodic peaks show splitting with a prewave followed by stripping peak. When the switching potential is changed to more cathodic values, stripping peak height increases indicating the increase in amount of cadmium deposited during the forward scan.

The voltammograms recorded from cyanide cadmium solutions containing 1 *M* free potassium cyanide are shown in Fig. 6B. Fig. 6A is the background curve in potassium cyanide solution. The prewave and sharp peak get combined to give a single characteristic stripping peak. The influence of free cyanide on cadmium deposition and dissolution from complex cyanide solution becomes clear when varying concentrations of potassium cyanide were introduced into the electrolyte. With increase in free cyanide

TABLE III: Cyclic voltammetric parameters for 0.5 M cadmium cyanide solution at 0.02 $Vsec^{-1}$

Concn of potassium cyanide (*M*)	E_d (V)	$E_{p,c}$ (V)	$I_{p,c}$ ($A.cm^{-2}$)	E_λ (V)	$E_{p,a1}$ (V)	$I_{p,a1}$ ($A.cm^{-2}$)	$E_{p,a2}$ (V)	$I_{p,a2}$ ($A.cm^{-2}$)
0	-1.150	-1.350	0.060	-1.400	-1.000	0.027	-0.870	0.051
	-1.150	-1.350	0.060	-1.600	-1.000	0.030	-0.850	0.075
	-1.150	-1.350	0.060	-1.800	-1.000	0.030	-0.830	0.099
0.30	-1.220	-1.380	0.060	-1.400	-1.000	0.039	-0.890	0.036
	-1.220	-1.380	0.060	-1.600	-1.020	0.042	-0.850	0.078
	-1.220	-1.380	0.060	-1.800	-1.020	0.048	-0.840	0.108
0.60	-1.240	-1.390	0.060	-1.400	-1.020	0.047	—	—
	-1.240	-1.390	0.060	-1.600	-1.020	0.063	-0.870	0.081
	-1.240	-1.390	0.060	-1.800	-1.020	0.066	-0.820	0.111
1.00	-1.280	-1.400	0.060	-1.400	-1.050	0.042	—	—
	-1.280	-1.400	0.060	-1.600	-1.030	0.075	—	—
	-1.280	-1.400	0.060	-1.800	-1.010	0.087	—	—
1.30	-1.300	-1.420	0.060	-1.400	-1.060	0.033	—	—
	-1.300	-1.420	0.060	-1.600	-1.020	0.093	—	—
	-1.300	-1.420	0.060	-1.800	-1.000	0.096	—	—

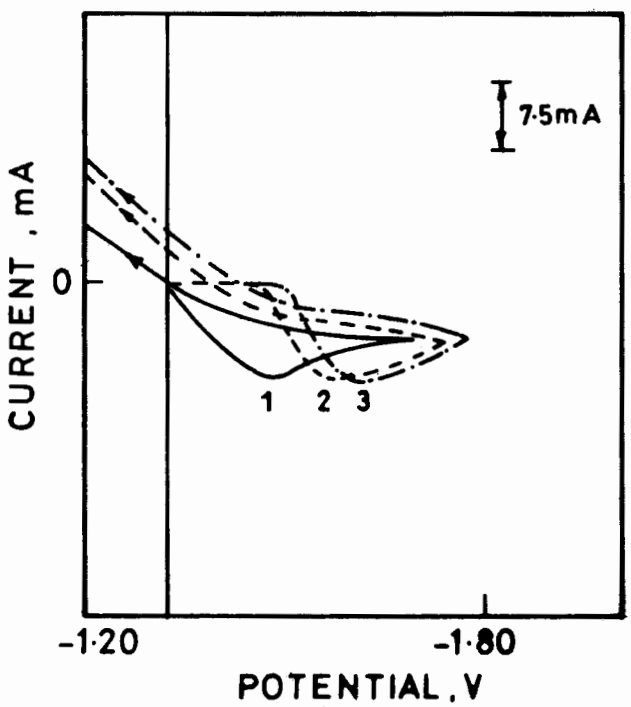

Fig. 7: Voltammograms of cadmium reduction on cadmium electrode v 0.02 $Vsec^{-1}$. solution 0.5 M cadmium as cyanide complex + Free KCN (1) 0 (2) 0.06 (3) 1 *M*

concentration there is a small increase in E_d (Table III) and $E_{p,c}$ but marked influence is visible in the anodic sweep voltammograms. As the free cyanide concentration increases, the prewave gains more importance and at sufficiently high concentration of KCN, only one dissolution peak is observed. This may be explained to be due to the fact that dissolution of cadmium occurs to give two different types of complex ions in varying valency states, sufficient excess of free cyanide is necessary to ensure that the normal cadmicyanide complex is predominantly obtained.

The cathodic shift of deposition potential and cathodic peak potential with increase in free KCN concentration could be observed for cadmium deposition on cadmium working electrode also (Fig. 7).

CONCLUSION

Voltammetric investigations have been used to understand the electrodeposition and dissolution

characteristics of cadmium from sulphate, sulphamate and cyanide solutions. The complexing effect of cyanide is visible in terms of cathodic shift of cathodic peak potentials and lowering of cathodic peak currents. The anodic stripping peaks show characteristic patterns depending on the switching potential and concentration of anion. From the anodic sweep voltammograms for cyanide containing solutions, the influence of free potassium cyanide in facilitating dissolution of cadmium in the specific complex state is clear.

REFERENCES

1. W H Safranek, *Plat Surf Finish,* **84-8** (1997) 45
2. *Metal Finishing Guide Book & Directory,* **95** (1997) 206
3. A M Abd El Halim and M I Sabahi, *Surf Techn,* **19-1** (1983) 45
4. G Akila, P Malathy, J Sobha, RM Krishnan, S Sriveeraraghavan and S R Natarajan, *Bull Electrochem,* **5-5** (1989) 328
5. L Serota, *Metal Finish,* **63-3** (1965) 73
6. K S Indira, K Vasantha and K S G Doss, *Metal Finish,* **66-3** (1968) 56
7. T Montiel, O Solorza and H Sanchez, *J Electrochem Soc,* **147-3** (2000) 1031
8. T S N Sankaranarayanan, *Metal Finish,* **97-6** (1999) 94
9. T C Franklin, T S N Sankaranarayanan and M Jackson, *J Electrochem Soc,* **145-3** (1998) 801