

ELECTROPLATING OF SILVER-CADMIUM ALLOYS

SOBHA JAYAKRISHNAN AND K I VASU*

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

* Surasa, Hebbal, Bangalore 560 024. INDIA

Silver cadmium alloys are reported to have increased hardness, electrical conductivity and tarnish resistance. Electroplated coatings of these alloys find applications as bearing alloy, non-tarnishing coating and electronic coating material. The standard electrode potentials of silver and cadmium are too far apart to permit co-deposition from simple salt solutions. Suitable complexing is necessary to bring the deposition potentials closer and permit codeposition. Various types of solutions have been investigated by the authors to explore the possibility of electroplating alloys with varying proportions of silver and cadmium and the results are presented in this paper. Electroplating experiments were carried out under varying concentrations of metal and operating conditions. Cyclic and stripping voltammetric techniques were employed. Characterisation of deposits were done by X-ray diffraction, scanning electron microscopy and microhardness measurements.

Keywords: Electroplating, Ag-Cd alloys, non-cyanide alkaline bath.

INTRODUCTION

Investigations on electroplating of alloys are gaining importance as alloy plating leads to the production of deposits with improved properties. Silver-cadmium alloys are reported [1-4] to have increased hardness, electrical conductivity and tarnish resistance. Electroplated coatings of these alloys find applications as bearing alloy, nontarnishing coating and electronic coating material.

The standard electrode potential of silver and cadmium are too far apart to permit codeposition from simple salt solutions. Suitable complexing is necessary to bring the deposition potentials closer and permit codeposition. Studies on deposition of silver-cadmium alloy from simple salt, thiocyanate, thiourea and cyanide solutions have been reported earlier [4-11]. A noncyanide alkaline bath based on thiosulphate for electrodeposition of silver has been reported by the authors [12,13]. Results of investigations on codeposition of cadmium with silver from thiosulphate based electrolytes are presented in this paper.

EXPERIMENTAL

Electroplating studies

Solutions used in this investigation are a) silver as thiosulphate 0.25 or 0.50 M containing sodium thiosulphate

1.0 M and sodium metabisulphite 0.2 M to which cadmium additions were made either as sulphate or b) cadmium as sulphate 0.50 M plus ammonium sulphate 0.50 M to which silver additions were made as thiosulphate complex along with sodium thiosulphate (1.0 M) and sodium metabisulphite (0.2 M).

Electroplating experiments were carried out on platinum cathodes (2 x 6 x 0.02 cm) using platinum foil of same size as anode. After weighing the plated deposit, it was stripped in 1:1 HNO₃ and analysed for silver content by thiocyanate method and cadmium by EDTA method [14,15]. Current efficiency calculations were made taking into consideration the percentage composition of the alloy also.

X-ray diffraction patterns of the deposits were recorded using XRD instrument JEOL with CuK_α radiation.

Voltammetric studies

Voltammetric studies were carried out in a two compartment three electrode cell using glassy carbon embedded in teflon sheath (exposed area 0.25 cm²) as working electrode, platinum foil as counter electrode (2 x 1 x 0.02 cm) and saturated calomel reference electrode.

Potential sweep programmes were executed using a potentiogalvanoscan (PGS81 Wenking) and the resulting current-voltage response recorded in an X-Y recorder (Rikadenki, RY-101 A).

TABLE I: Effect of addition of cadmium to thiosulphate silver bath with 0.5 M silver, pH 4.5, c.d. 1 A/dm²

Cadmium concn	Cadmium added as sulphate	Cadmium added as sulphamate		
Deposit nature	Cadmium content (wt%)	Deposit nature	Cadmium content (wt%)	
0.00	White	----	----	
0.25	White	----	White	
0.50	Dull white	5.2	Dull white	5.0
0.75	**	22.0	**	21.0
1.00	***	28.7	***	27.5

** = Dull white with a powdery non-adherent top layer

*** = Grey with thick non-adherent top layer

RESULTS AND DISCUSSION

Electroplating investigations

Influence of adding cadmium to solutions containing 0.5 M silver as thiosulphate complex

Cadmium additions were made either as sulphate or sulphamate to a thiosulphate silver bath containing 0.5 M silver as thiosulphate along with sodium thiosulphate 1.0 M and sodium metabisulphite 0.2 M. Smooth silvery white deposits are obtained (Table I) at 0.25 M cadmium with no incorporation of cadmium in the deposit. At 0.5 M cadmium in the bath, dull deposits with 5% cadmium inclusion are obtained. Alloys with higher cadmium content (21-29%) obtained at 0.75 and 1.0 M cadmium concentration, are

TABLE II: Cathode current efficiency and percentage cadmium in deposit for thiosulphate silver (0.5 M) bath containing cadmium sulphate at 1 A/dm², duration 30 mts, pH 4.5

Concn of cadmium (M)	Nature of deposit	Weight of deposit (g/10 cm ²)	C.C.E (%)	Cadmium content in deposit (wt%)
0.00	White	0.197	98.0	-----
0.20	White	0.195	96.9	-----
0.25	White	0.193	95.9	-----
0.30	Dull white	0.190	94.8	0.5
0.35	Dull white	0.180	90.4	1.2
0.43	Dull white	0.173	88.1	3.0
0.50	Dull white	0.168	87.5	5.2
0.60	**	0.130	71.7	12.0
0.70	**	0.120	69.7	18.3
0.80	***	0.098	60.0	24.5
1.00	***	0.090	56.5	28.7

** = Grey with thin powdery top layer

*** = Thick non-adherent top layer

TABLE III: Influence of c.d. and cadmium concentration on silver-cadmium alloy deposition from thiosulphate silver bath (0.25 M) pH 4.5

Concn of cadmium (M)	C.D (A/dm ²)	Nature of deposit	CCE (%)	Cadmium content in deposit (wt%)
0.25	0.25	White	90.0	-----
	0.50	***	50.0	-----
	0.75	***	20.0	-----
	0.25	White	87.6	-----
	0.50	Dull white	87.0	1.7
	0.75	Dull white	66.1	5.0
	1.00	***	9.6	8.2
	0.25	Dull white	85.0	2.3
	0.50	***	50.1	7.0
	0.75	***	16.9	14.2
0.50	1.00	***	10.6	20.0
	0.25	Dull white	70.0	4.5
	0.50	***	33.4	13.2
	0.75	***	15.0	20.2
1.00	1.00	***	9.6	30.8

*** = Dull white with grey surface film

found to be dull white or grey with powdery non adherent surface layer. Results are almost similar whether cadmium is added as sulphate or sulphamate (Table I).

Starting from thiosulphate silver solution, gradual additions of cadmium sulphate were made and deposits obtained at 1 A/dm² c.d. Nature of the deposits, deposition efficiency and cadmium content are found to show a behaviour as shown in Table II. Smooth white silver deposits with no cadmium incorporation are obtained upto 0.25 M cadmium in the bath. At 0.30-0.50 M cadmium, dull white alloy deposits with 0.5-5.0% cadmium inclusion are obtained. An increase in cadmium concentration above 0.50 M produces

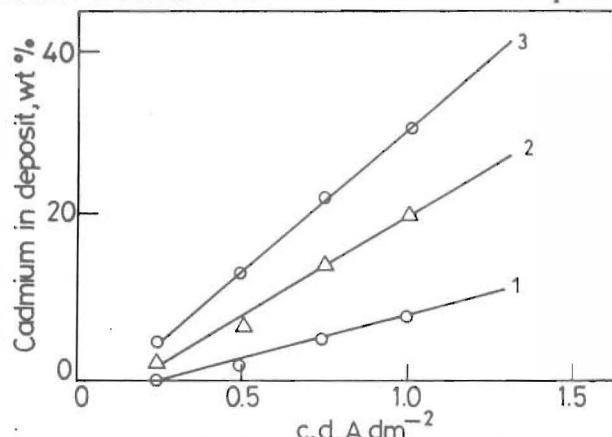


Fig. 1: Influence of c.d. on Cd content of electrodeposits from 0.25 M silver thiosulphate bath containing Cd as sulphate
(1) 0.25 (2) 0.50 (3) 1 M

deposits with powdery top layer, but the thin grey adherent layer shows high cadmium contents.

Influence of addition cadmium sulphate to solutions with 0.25 M silver as thiosulphate complex

Results of plating experiments at varying current density from silver thiosulphate solutions (0.25 M) containing 0.50 M sodium thiosulphate and 0.2 M sodium metabisulphite to which varying concentrations of cadmium are added are shown in Table III. Alloys with varying cadmium contents are plated from this solution. Deposits with upto 5% cadmium are white and adherent whereas at higher cadmium contents, deposits become dull and grey coated with nonadherent powdery top layer. Current density plays a very important role in codeposition (Table III, Fig. 1). Increase in c.d results in deposits containing higher cadmium content. However, higher c.d appears to be unfavourable for alloy deposition which gets deposited in burnt form or as hydroxide resulting in the formation of non adherent top layer.

Fig. 2, curve 1 shows the relationship between cadmium concentration in the bath and cadmium content in the alloy. The curve is characterised by an initial slow increase in cadmium content followed by a sudden steep increase. It is observed that the cadmium deposits produced during the initial slow increase region alone are adherent deposits whereas at regions within and after the steep increase deposits have a nonadherent top layer.

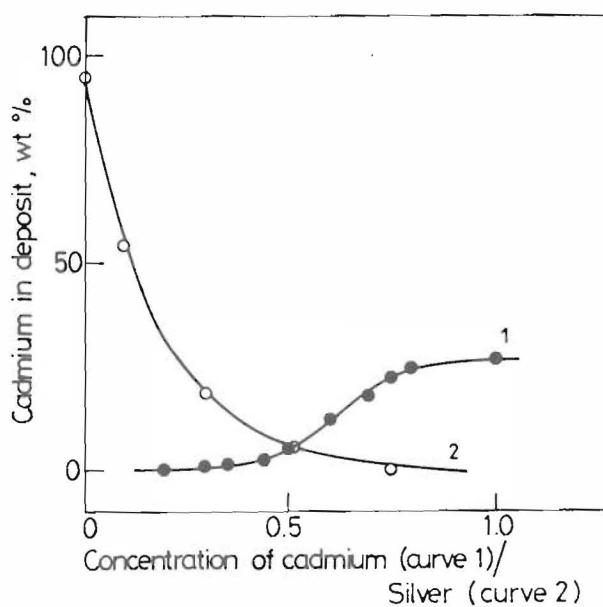


Fig. 2: Influence of addition of
(1) Cadmium to 0.5 M silver thiosulphate
(2) Silver to 0.5 M cadmium sulphate on
cadmium content of alloy deposits

TABLE IV: Effect of adding silver as thiosulphate complex to cadmium sulphate baths
pH 4.5, c.d. 1 A/dm²

Bath type	Concn of silver (M)	Concn of cadmium (M)	Nature of deposit	Cadmium content in deposit (wt%)
Cadmium as sulphate	0.00	0.50	*	100.0
	0.01	0.50	*	95.0
	0.10	0.50	**	54.0
	0.30	0.50	**	18.0
	0.50	0.50	Dull white	5.2
	0.75	0.50	White	0.0
Cadmium as sulphate + 2g lit ⁻¹	0.00	0.50	Uniform white	100.0
	0.15	0.35	***	40.2
	0.25	0.25	***	8.0
CTAB	0.50	0.25	Dull white	0.0
	0.50	0.50	Dull white	5.0
	0.50	0.75	***	20.6

* = Non-uniform powdery deposit

** = Grey deposit with non-adherent surface layer

*** = Grey deposit with non-adherent top layer

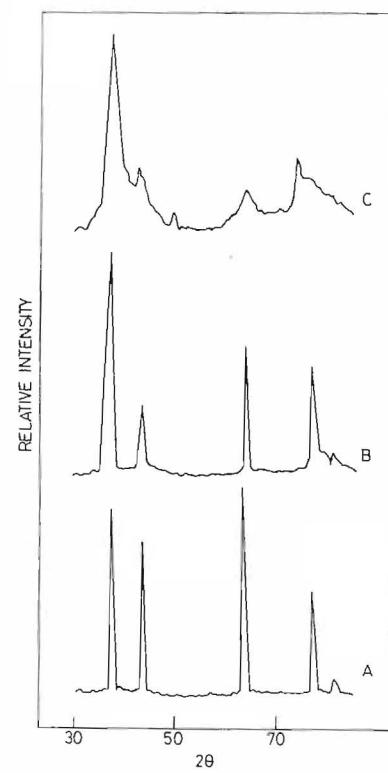


Fig. 3: XRD patterns of silver and silver-cadmium alloys electrodeposited from thiosulphate bath.
Cd content in the alloys (A) 0 (B) 5 (C) 12%

Influence of adding silver thiosulphate to solutions with 0.50 M cadmium as sulphate

Effect of silver addition to cadmium baths were observed (Table IV, Fig. 2, Curve 2) by adding silver as thiosulphate complex along with sodium thiosulphate and sodium metabisulphite to cadmium sulphate solution. Alloy deposits with cadmium higher than 5% are found to be grey in appearance with a nonadherent top layer. Sound deposits are obtained upto 5% cadmium in the alloy.

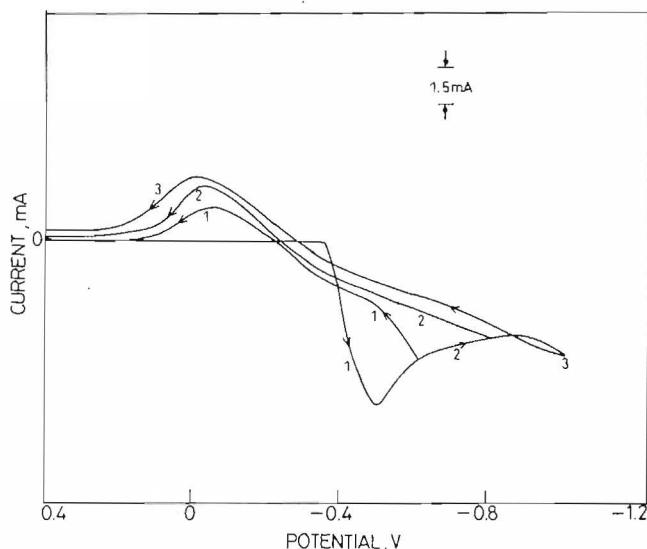
Cetyl trimethyl ammonium bromide (CTAB), an addition agent recommended [16] in cadmium plating baths was tried as an additive. Results (Table IV) show that though CTAB has a smoothening effect on pure cadmium deposition it does not influence alloy deposition. The percentage composition of the alloy as well as the nature of the alloy remain unaltered in presence of this additive.

XRD studies of silver-cadmium electrodeposits

XRD patterns of Ag-Cd deposits obtained from thiosulphate solutions are shown in Fig. 3. The pattern obtained for alloys with upto 5% cadmium show peaks similar to silver, with slight shift in 2θ values indicating the formation of solid solutions of cadmium in silver. Alloys with higher cadmium contents give very broad peaks indicating the noncrystalline nature of the deposits.

Voltammetric investigations

The results of cyclic and anodic sweep voltammetric studies were analysed using considerations similar to those suggested in recent literature [17-21]. Cathodic linear sweep



*Fig. 4: Cyclic voltammogram from thiosulphate silver (0.5 M) solution on glassy carbon electrode
Scan rate: 0.02 V/sec
Switching potential (1) -0.60 (2) -0.80 (3) -1.00 V*

voltammograms show two peaks corresponding to electrodeposition of the two metals. During the anodic cycle, the number of peaks obtained depends on the switching potential, thereby indicating the potential control of the alloy deposition process. In the anodic sweep voltammetric experiments, the deposition was carried out at controlled potential followed by stripping of the alloy by sweeping towards anodic potentials. The number and characteristics of the stripping peaks are found to be indicative of the nature of the electrodeposited alloy.

Cyclic voltammograms obtained from thiosulphate silver solutions (0.5 M) (Fig. 4) show single cathodic and anodic peaks with the area under anodic peak increasing as switching potential becomes more negative. This is indicating the higher amount of metal deposition as we sweep to more cathodic potentials. Anodic stripping voltammograms from 0.5 M silver thiosulphate solution show (Fig. 5a) that there is an increase in anodic peak height and area under peak when deposition potential changes from -0.60 to -0.80 V, but at more negative deposition potentials the peak height decreases. This can be explained to be due to the fact that the competing reaction of hydrogen evolution results in decrease of silver deposition efficiency. This is in conformity with the observation during plating studies that at high deposition c.d only thin deposits with low cathode

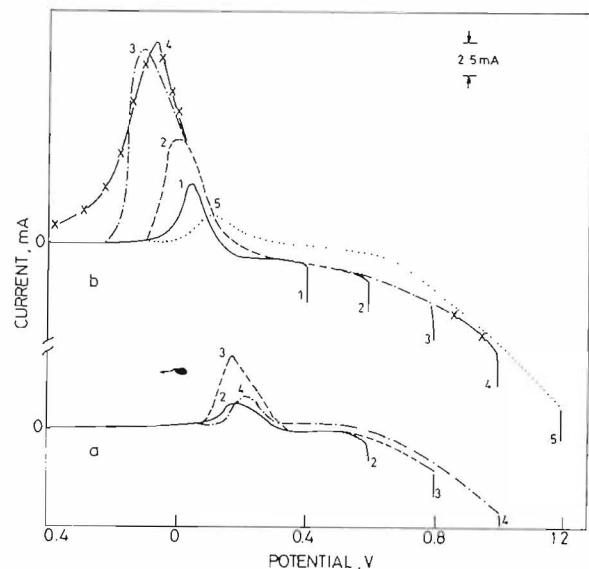


Fig. 5: Stripping voltammograms of silver and silver-cadmium alloys electrodeposited from (a) 0.5 M silver thiosulphate solution (b) a + 0.8 M cadmium sulphate at various deposition potentials (1) -0.40 (2) -0.60 (3) -0.80 (4) -1.00 (5) -1.20 V

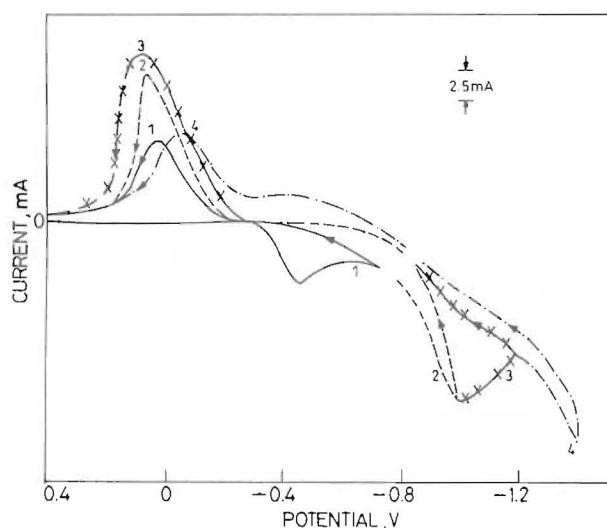


Fig. 6: Cyclic voltammogram from thiosulphate silver (0.5 M) solution containing 0.8 M cadmium sulphate

Scan rate: 0.02 V/sec

Switching potential (1) -0.80 (2) -1.00 (3) -1.20 (4) -1.40 V

current efficiency percentages are obtained (Table III). These thin deposits have nonadherent surface films which may be due to the formation of silver oxide and sulphide resulting from bath decomposition as a result of the high pH near the cathode.

Fig. 6 shows the cyclic voltammetric response from a 0.5 M silver thiosulphate solution containing 0.8 M cadmium sulphate. Two cathodic peaks corresponding to silver and cadmium reductions are observed. When switching potentials is less than -1.2 V , a single anodic peak at potentials comparable to the silver reduction peak of figure 5 but of increased peak height, is obtained indicating the deposition of silver-cadmium alloy of the solid solution type. When switching potentials are more cathodic, additional peaks at more negative potentials are observed which indicate the possibility of depositing higher cadmium content alloys belonging to other phases. Results of anodic stripping voltammetric experiments (Fig. 5b) also lead to similar conclusions. When deposition potential is gradually made more cathodic, the stripping peaks show increased peak area without considerable variation in the peak potential indicating the formation of solid solutions with varying cadmium contents. But at cathodic deposition potentials of 1.0 V very shallow stripping peaks extending to more electronegative potentials are obtained. This shows that as the deposition potential is increased to achieve conditions favourable for formation of cadmium rich phases, efficiency of deposition is reduced considerably. These appear to be

the conditions under which formation of silver oxide and sulphide results in nonadherent grey surface films.

The conclusion from the above studies is that the thiosulphate solution is capable of producing only silver-cadmium alloys of the solid solution type. Condition favouring higher cadmium content is deposition at more cathodic potential, but this results in production of only thin films.

CONCLUSION

The possibility of codepositing cadmium with silver from a thiosulphate complexed silver solution was investigated by electroplating experiments combined with XRD studies and also by cyclic voltammetric and anodic sweep voltammetric investigations. But methods of approach give identical conclusions: the thiosulphate solution is capable of producing silver-cadmium alloys of the solid solution type in acceptable form. When cadmium contents are higher, deposits with nonadherent surface films are obtained.

REFERENCES

1. L W Flott, *Metal Finishing*, **83-7** (1985) 11
2. S Koichi, *Jap Pat*, 2 159 327 (1990)
3. L Addicks, *Silver in Industry*, Reinhold Publishing Corporation, USA (1940)
4. A Brenner, *Electrodeposition of Alloys*, Academic Press, NY (1963)
5. C W Stillwell and L E Stout, *J Amer Chem Soc*, **54-7** (1932) 2583
6. C W Stillwell, *Metal Ind*, **31** (1933) 47
7. C W Stillwell and H I Feinberg, *J Amer Chem Soc*, **55** (1933) 1864
8. C L Faust, D J Henry and W G France, *Trans Electrochem Soc*, **72** (1937) 479
9. F C Mathers and A D Johnson, *Trans Electrochem Soc*, **74** (1938) 229
10. C L Faust, *Trans Electrochem Soc*, **78** (1940) 383
11. I Nambissan and A J Allmand, *Trans Faraday T*, **47** (1951) 303
12. Sobha Jayakrishnan, S R Natarajan and K I Vasu, *Bull Electrochem*, **9** (8-10) (1993) 459
13. Sobha Jayakrishnan, S R Natarajan and K I Vasu, *Trans SAEST*, **31** (1-2) (1996) 1
14. A I Vogel, *A Textbook of Quantitative Inorganic Analysis*, Longmans Green and Co., London (1951)
15. P W Wild, *Modern Analysis for Electroplating*, Finishing Publications Ltd., England (1974)
16. K S Indira, K Vasantha and K S G Doss, *Metal Finishing*, **66-2** (1968) 49
17. V M Lopez Hirata and E M Aree Estrada, *Electrochim Acta*, **42-1** (1997) 61
18. E Gomez and E Valles, *J Electroanal Chem*, **421** (1997) 157
19. J Crouzier and I Bimaghra, *J Appl Electrochem*, **23** (1993) 775
20. V D Jovic, A R Despic, J S Stevanovic and S Spaic, *Electrochimica Acta*, **34-8** (1989) 1093
21. S Swathirajan, *J Electrochim Soc*, **133-4** (1986) 671