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Effect of some plating variables on the electrodeposition of Cu-Zn alloys from alkaline tartrate baths

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The electrodeposition of copper, zinc and copper–zinc alloys from alkaline tartrate solutions has been investigated under different conditions of bath composition, added ammonium chloride, current density and temperature. A detailed study has been made of the effect of the variables on the cathode potentials and cathode efficiencies of copper, zinc and Cu–Zn alloys; the compositions of the alloys were determined. The results were consistent with the behaviour of a regular alloy plating system with zinc being the less noble metal.

1. Introduction

Although Cu–Zn alloys are commercially electrodeposited from a cyanide bath [1, 2], a number of other, non-cyanide plating baths have been investigated. Stabrovsky [3] and Ray *et al.* [4] electrodeposited brass from a copper (II) glycerate–zincate bath. Stabrovsky [5], de Kay Thompson [6], Rama Char *et al.* [7, 8], and Persiantseva and Titov [9] investigated the deposition of brass from a pyrophosphate bath. Sadagobachari *et al.* [10], and Nesmeyanova *et al.* [11] studied the plating of brass from a triethanolamine bath.

An alkaline tartrate bath in which copper is present as a copper (II) tartrate complex and zinc as zincate appears to have commercial possibilities. This bath which has not received much study was first mentioned by de Kay Thompson [6] and later investigated by Sukhodskii *et al.* [12]. Ray and Banerjee [13] studied this bath, but did not give its exact composition. Therefore, it seems interesting to investigate the electrodeposition of pure copper, zinc and Cu–Zn alloys from this bath under different experimental conditions.

It is known [14] that in the presence of tartrate, copper ions form complexes; at pH > 10 the predominant composition of the complex ion is $(Cu(OH)_2C_4H_4O_6)^{2-}$ with $K_{inst} = 7{\cdot}3 \times 10^{-20}$. In the pH range of 5·5 to 11 and in the presence of tartrate, the zinc ions form a complex ion of the composition $(Zn(OH)C_4H_4O_6)^-$, having $K_{inst} = 2{\cdot}4 \times 10^{-8}$, and at pH > 11 the zincate ion $Zn(OH)_3^-$, having $K_{inst} = 3 \times 10^{-16}$, is predominantly formed [15].

2. Experimental

All plating solutions and reagents used were made of Analar chemicals and doubly distilled water. In order to facilitate references, a symbol was given to each bath to identify it and to designate its constituents, Table 1. The pH was measured

Table 1. Composition of baths

Bath	*$CuSO_4$*	*$ZnSO_4$*	*NaK-tartrate*	*NaOH*	*NH_4Cl*
Cu-1	0·30		0·70	2·50	
Cu-2	0·15		0·70	2·50	
Cu-3	0·15		1·20	2·50	
Cu-4	0·15		1·20	3·00	
Cu-5	0·30		0·70	2·50	0·06
Zn-1		0·20	0·70	2·50	
Zn-2		0·10	0·70	1·80	
Zn-3		0·10	0·70	2·50	
Zn-4		0·20	0·70	2·50	0·06
Cu–Zn-1	0·30	0·20	0·70	2·50	
Cu–Zn-2	0·20	0·20	0·70	2·50	
Cu–Zn-3	0·20	0·10	0·70	2·50	
Cu–Zn-4	0·20	0·20	1·20	2·50	
Cu–Zn-5	0·20	0·10	0·70	1·80	
Cu–Zn-6	0·30	0·20	0·70	2·50	0·06

The concentration of all constituents is expressed in $mol\,l^{-1}$.

with a glass electrode. In all solutions, the pH was 12·90 ± 0·15.

The electrolytic cell used consisted of two equal compartments separated by a sintered glass disc. For each run, 200 ml of fresh solution was introduced into the cell. A Pt sheet cathode (1·6 cm^2) was placed in the cathode compartment and a Pt wire anode was placed in the anode compartment. The quantity of electricity passed during plating was checked by means of a copper coulometer which was connected in series with the cell. The solution temperature was maintained within ± 0·5° C. The plating time was 20 min. No agitation was provided during the plating. Each run was performed at least twice. The cathode efficiency of alloys was determined by a recommended method [16]. The alloy deposit was stripped from the cathode with 1 : 1 dilute nitric acid and subsequently analysed to ascertain the copper and zinc contents of the deposit [17].

The cathode potential was measured relative to a saturated calomel electrode which was connected to the test electrode via a bridge filled with the solution to avoid contamination. The potential was recorded by using a potentiometer (Radiometer PHM 62).

3. Results and discussion

3.1. *Cathode potential*

Fig. 1 represents the potential–current density curves of copper from the selected baths at 27° C. In general, the polarization increased with rising current density; concentration polarization was the most important in these solutions. The curves have inflections corresponding to the potentials of copper discharge from the main type of complex ion. Increasing the copper content in the bath shifted the polarization curves in the less negative direction. Upon increase of the concentration of tartrate salt, the polarization curve shifted in the more negative direction. This result is apparently due to the increase in the stability of the copper tartrate complex with increasing concentration of the complexing agent. The figure shows that NaOH has a similar effect on the cathode polarization of copper, since increas-

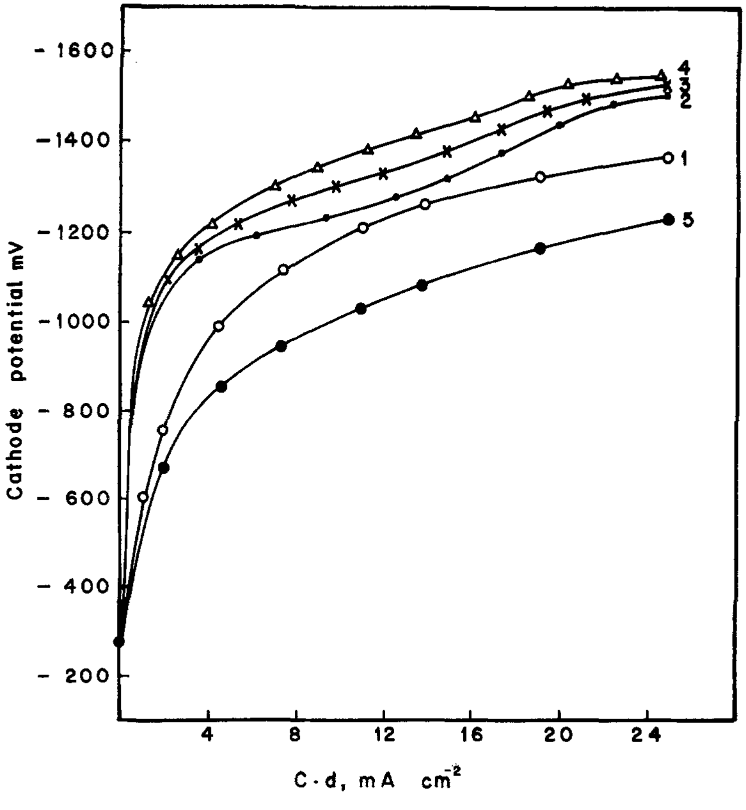

Fig. 1. Cathode potential curves of copper at 27° C. (1) Cu-1 bath; (2) Cu-2 bath; (3) Cu-3 bath; (4) Cu-4 bath; (5) Cu-5 bath.

ing the concentration of caustic soda shifted the curve in the more negative direction. Addition of NH_4Cl to the bath exerted a polarization decreasing effect. The depolarization could be attributed to the presence of chloride ions in the solution; the chloride ions may be adsorbed on the positive side of the zero charge potential so as to decrease the effective energy of activation of metal deposition [18].

Fig. 2 shows the potential–current density curves of zinc from the selected solutions at 27° C. The deposition of zinc from solutions was characterized by a large polarization, due mainly to the concentration polarization resulting from the complexing of the zinc ions. Increasing the zinc content or the addition of NH_4Cl shifted the polarization in the less negative direction. On the other hand, the reverse effect was observed on increasing the concentration of NaOH. This is probably due to the increase in the stability of zincate complexes from which zinc is predominantly discharged.

By comparing the polarization curves of the parent metals, we deduced that the static potential of copper was much more positive than that of zinc. On electrolysis, the copper deposition was attended by larger polarization than that of zinc; therefore, the potentials of the two metals were brought sufficiently close together to permit co-deposition. However, under similar conditions, the copper polarization was still more positive than that of zinc.

The potential–current density curves for the deposition of the alloys were traced under different experimental conditions. Some of the results are presented in Fig. 3. It was found that increasing the concentration of tartrate or NaOH shifted the polarization curve in the more negative direction, while addition of NH_4Cl or raising the temperature shifted it in the less negative direction. Fig. 4 shows that the alloy curve lies between the experimental curves of the parent metals. This indicates that copper was discharged into the alloy at more negative and zinc at more positive potentials than in separate deposition.

From the potential curves of the alloy and its composition, we can determine the proportion of the current that was used in the deposition of each metal and plot the corresponding potential curve for each. Such studies are rare, and the

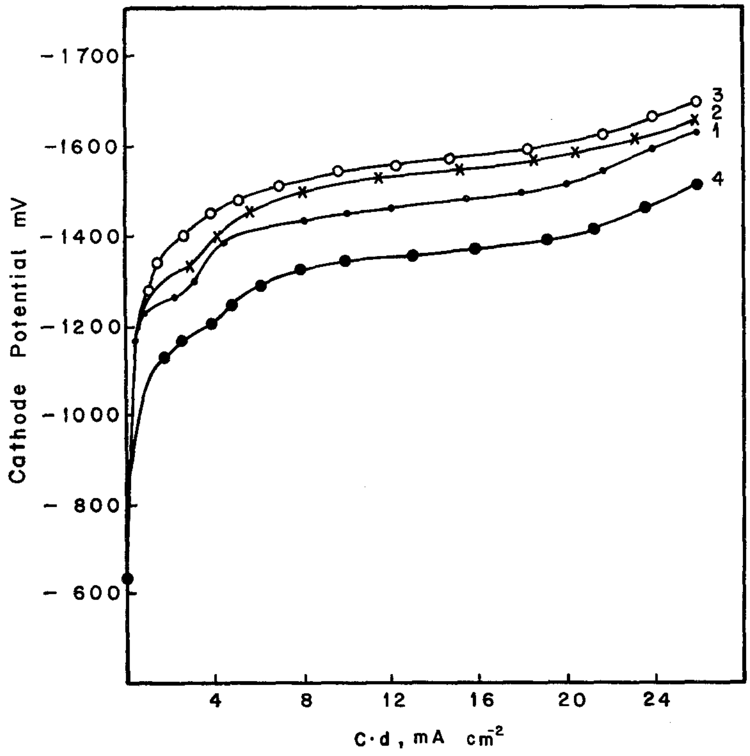

Fig. 2. Cathode potential curves of zinc at 27° C. (1) Zn-1 bath; (2) Zn-2 bath; (3) Zn-3 bath; (4) Zn-4 bath.

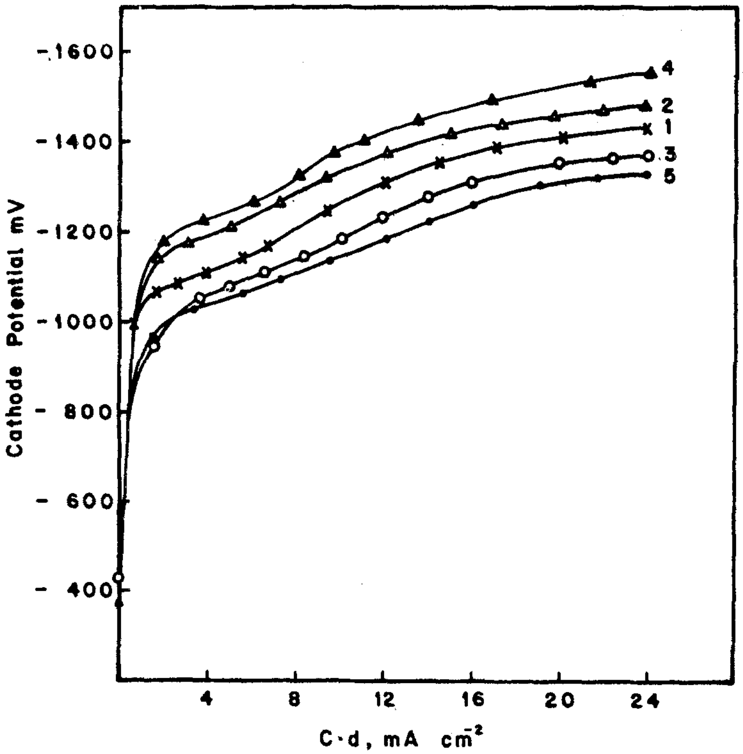

Fig. 3. Cathode potential curves of Cu–Zn alloy.
(1) Cu–Zn-1 bath, 27° C;
(2) Cu–Zn-2 bath, 27° C;
(3) Cu–Zn-6 bath, 27° C;
(4) Cu–Zn-4 bath, 27° C;
(5) Cu–Zn-1 bath, 50° C.

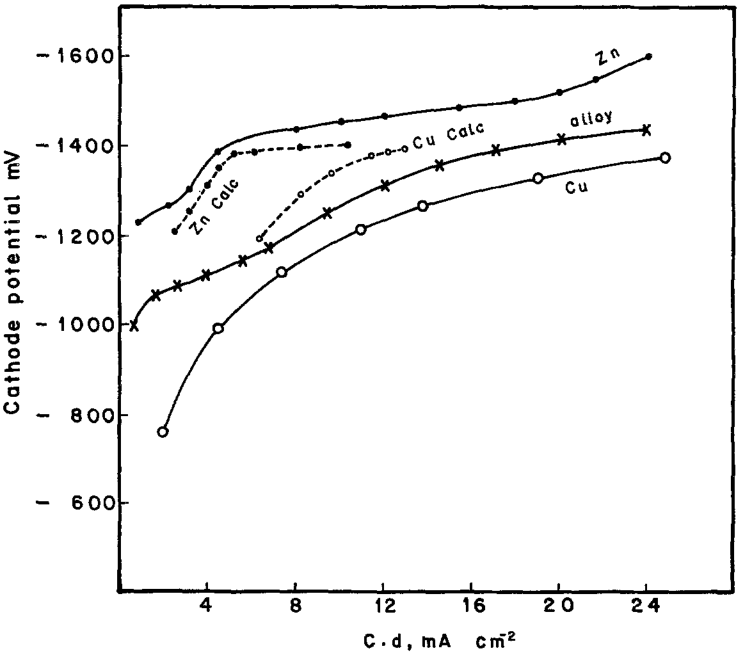

Fig. 4. Reconstruction of single metal potential curves from alloy composition and potential, at 27° C. Cu from Cu-1 bath; Zn from Zn-1 bath; alloy from Cu–Zn-1 bath.

metal ratios in the deposit have been found to deviate widely from those predicted from the single metal potential curves [19, 20]. Fig. 4 gives a typical example of the calculated partial current density–potential curves of copper and zinc in co-deposition. For comparison, the experimental curves of the individual metals and the alloy are included. The figure shows the shifts in the polarization of the two metals that have occurred as a result of co-deposition. The two calculated curves become closer, indicating the possibility of obtaining alloys of different composition by varying the plating conditions. Both calculated and experimental curves of copper are closer to that of the alloy indicating that a high copper alloy is to be expected at low current densities, in agreement with the results obtained.

3.2. *Cathode efficiency*

The cathode efficiencies of pure copper, zinc and the alloy were determined and the results are presented in Figs. 5–7, respectively. The cathode efficiency of copper decreased with increasing current density but increased with rising copper content in the bath. In all cases and at low current densities, the efficiency of copper deposition was above 100%. This may be due to the precipitation of basic compounds and their subsequent incorporation in the deposit [3].

In contrast to copper, the cathode efficiency of zinc increased with rising current density. At a given current density, the efficiency increased with rising zinc content in the bath, but decreased with increasing concentration of NaOH or the addition of NH_4Cl.

The cathode efficiency of the alloy deposition decreased with increasing current density. Under similar conditions, the co-deposition efficiency exceeded that of the single deposition of zinc. The variation of the cathode efficiency of co-deposition was due to the fact that the efficiency of single deposition of each metal has changed in the opposite sense with current density. The decrease in co-deposition efficiency is apparently due to the decrease in the individual cathode efficiency of copper deposition. The data also reveal that increasing the metal content in the bath increased the co-deposition efficiency. This result could be explained on the basis that increasing the metal content in the individual bath enhances its cathode efficiency through the decrease in cathode polarization.

3.3. *Alloy composition*

The effect of the plating variables on the composition of the alloy was determined. Figs. 8 and 9 show the percentage of zinc content (the less noble metal) in the deposit as a function of current density. Generally, the zinc content of the deposit increased with rising current density, reflecting the increase in the rate of deposition of the less noble metal. The results are characteristic of a regular alloy plating system [16]. The zinc content in the deposit increased with rising zinc concentration and with decreasing copper concentration in the bath. This result could be explained on the basis that the cathode efficiency of the individual

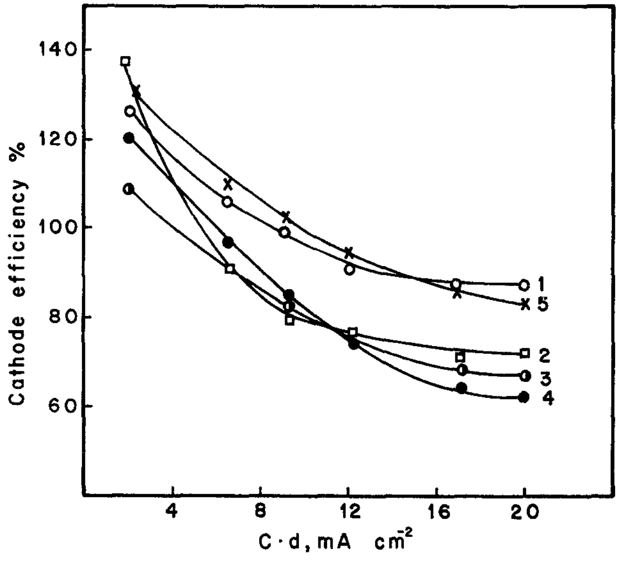

Fig. 5. Cathode efficiency curves of copper at 27° C. Legends are the same as in Fig. 1.

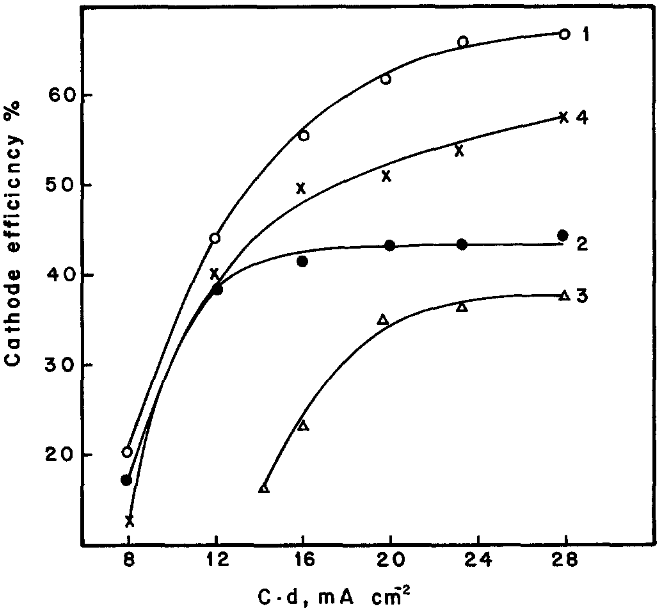

Fig. 6. Cathode efficiency curves of zinc at 27° C. Legends are the same as in Fig. 2.

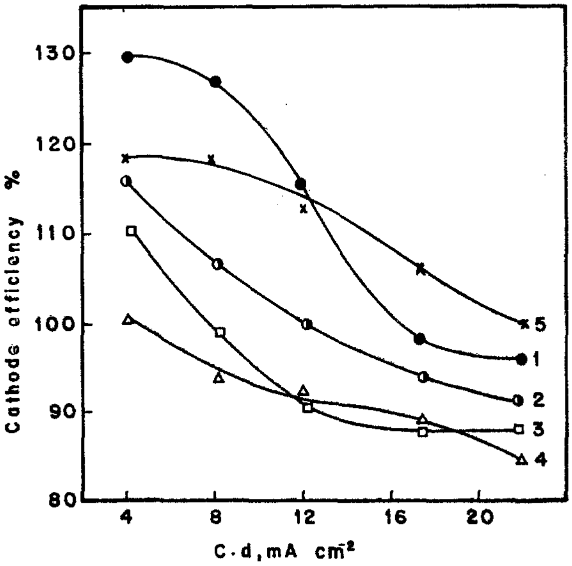

Fig. 7. Cathode efficiency curves of Cu–Zn alloy at 27° C. (1) Cu–Zn-1 bath; (2) Cu–Zn-2 bath; (3) Cu–Zn-3 bath; (4) Cu–Zn-4 bath; (5) (5) Cu–Zn-6 bath.

deposition of the two metals increased with increase of the contents of their ions in the bath. The zinc content of the deposit also increased with rising concentration of tartrate or NaOH, but decreased with the addition of HN_4Cl.

The effect of temperature on the composition of the alloy is illustrated in Fig. 9. An increase in temperature decreased the zinc content of the deposit. This trend of zinc content with temperature is also consistent with the behaviour of regular alloy plating systems. An increase in temperature increases the concentration of metal in the cathode diffusion layer [16]. An increase in the metal concentration at the solution cathode interface favours the increased deposition of copper (the more noble metal) which is depositing preferentially.

Fine-grained and highly adherent deposits were obtained in most cases. The colours of the deposits changed from red to yellow with increasing

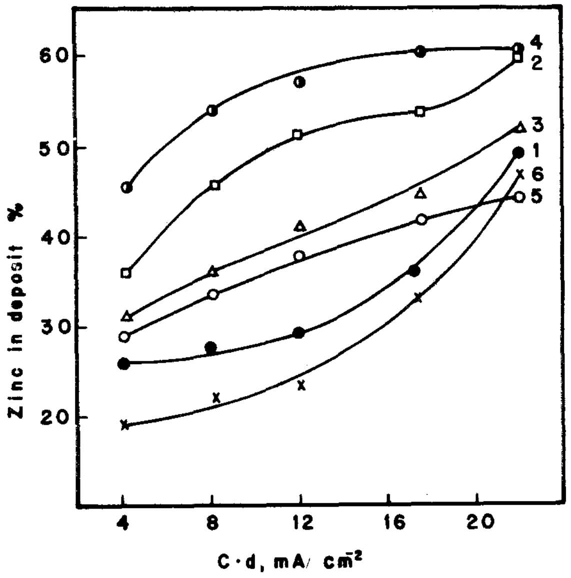

Fig. 8. Effect of bath composition on zinc content of deposit at 27° C. (1) Cu–Zn-1 bath; (2) Cu–Zn-2 bath; (3) Cu–Zn-3 bath; (4) Cu–Zn-4 bath; (5) Cu–Zn-5 bath; (6) Cu–Zn-6 bath.

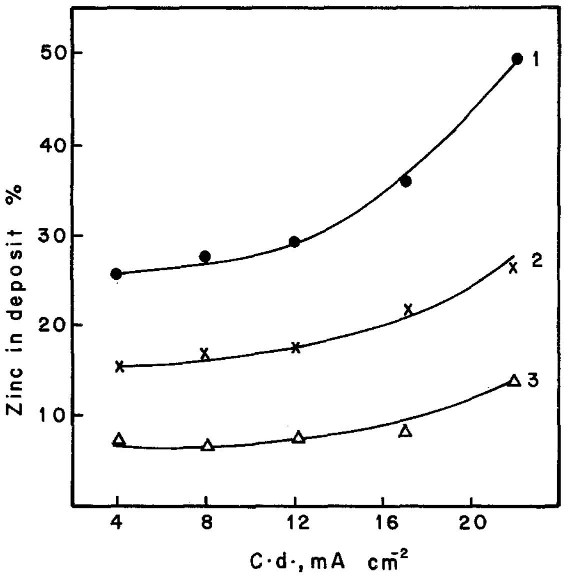

Fig. 9. Effect of temperature on zinc content of deposit, Cu–Zn-1 bath. (1) 27° C; (2) 35° C; (3) 50° C.

zinc content in the deposit. The addition of NH_4Cl improved the appearance of the deposit and also changed the colour from red to yellow.

References

[1] H. P. Coats, *Trans. Electrochem. Soc.* **80** (1941) 445.

[2] S. Buchan, 'Rubber to Metal Bonding', 2nd ed. Crosby Lockwood, London (1959).

[3] A. I. Stabrovsky, *Zhur. priklad. Khim.* **25** (1952). 968

[4] S. K. Ray, H. V. Udupa and B. B. Dey, *J. Sci. Ind. Res.* **14B** (1955) 652.

[5] A. I. Stabrovsky, *Zhur. fiz. Khim.* **26** (1952). 949:

[6] M. de Kay Thompson, *Met. Chem. Eng.* **10** (1912). 458.

[7] T. L. Rama Char and V. Sree, *J. Sci. Ind. Res.* **16A** (1957) 325.

[8] *Idem, Electroplating Met. Finishing* **12** (1959) 326.

[9] V. P. Persiantseva and P. S. Titov. *Chem. Abs.* **53** (1959) 912.

[10] R. Sadagobachari, N. B. Shivaraman and T. L. Rama Char, *Current Sci.* **20** (1951) 154.

[11] K. A. Nesmeyanova, S. A. Gintsberg and S. M. Gorelik, *Trudy Gosudarst. Nauch-Issledovatel. Ints. Khim. Prom.* **3** (1955) 46.

[12] V. A. Sukhodskii, V. L. Kheifetz and I. N. Chapurskii, *Soobshcheniya Tsentral' nyi Inst. (Leningrad)* **17** (1934) 209.

[13] S. K. Ray and T. Banerjee, *J. Sci. Ind. Res.* **12B** (1953) 438.

[14] M. E. Tsimbler, *Ukr. Khim. Zh.* **17** (1951) 3.

[15] I. K. Vitchenko and A. S. Tikhohov, *Tr. Voronezhsk Gos. Univ.* **32** (1953) 129.

[16] A. Brenner, 'Electrodeposition of Alloys', Vol. 1, Academic Press, New York (1963).

[17] G. Schwarzenbach and H. Gysling, *Helv. Chim. Acta* **32** (1949) 1108.

[18] M. A. Loshkarev, A. A. Kryukova, Y. M. Loshkarev and T. F. Dyachenko, *Electrochim. Acta* **9** (1964) 1119.

[19] Yu. V. Baimakov, *Trudy Leningrad. Polytekh. Inst. im M. I. Kalinia, Electromet, Tsvetnykh Metal* **188** (1957) 162.

[20] T. L. Rama Char, *Electroplating (India)* **1** (1959) 165.