Superimposition of Alternating Current on Electrodeposition of Cu-Cd Alloys in Presence of Chloride Ions

C.A. NOUBI, H. MANSOUR AND F.M. EL-CHEIKH
Chem. Dept, Faculty of Science (Quna and Assiut), Assiut Univ. Egypt.

Addition of chloride ions to the electrodeposition baths of Cu,Cd and Cu-Cd alloy affects the quality of deposit. Chloride ions also decrease the throwing power and increase the percentage of Cd in the alloy in the absence of surface active substances. Opposite effect was noticed in their presence. Superimposition of alternating current on the direct current applied for the deposition of the alloy was accompanied by a corresponding increase in the values of the throwing power of the electrolytes and a decrease of cadmium content in the alloy up to a certain limit of frequency (150 HZ), although, above this limit, the cadmium content started to increase again. In addition low frequencies of A.C. renders the deposite smoother whereas high frequencies do not affect the quality of the deposit.

The application of alternative current to the electrodeposition of metals has been investigated by Vagramyan and Soutagina[1] , the first to study the effect of alternating current of different types on the electrocrystallization of metals. Sisev[2] studied the ability of A.C. to improve the quality of the deposited alloy and the throwing power of the electrolytes.

The aim of the present work has been to study the effect of alternating current on the electrodeposition of Cu-Cd alloy in presence of chloride ions. The quality of the deposited alloy, its composition, and the throwing power of its electrolytes were thus the object of the present study.

EXPERIMENTAL

The electrolytic Cu-Cd alloys were deposited on a platinum sheet of 22.5cm^2 surface area. Separate copper and cadmium anodes were used. The deposited alloy was analysed; cadmium complexometrically and copper by iodimetric method[3].

The effect of the different variables on the quality and composition of the alloy was studied from the following baths:

A: $CuSO_4$. 5 H_2O (0.1 M) + $CdSO_4$. 8/3 H_2O (0.25 M) + CH_3COOH (1.0 M).
B: A + 0.8 M NH_4OH.
C: A + 0.0013 M sodium - naphthalene acetate (S.A.S.).
D: B + 0.0013 M sodium - naphthalene acetate
E: A,B or C + x M chloride ions, where x = 0.1, 0.25, 0.5 and 0.75 M

C.C.D. 0.5 A/dc^2 A.C. frequency 20 - 500 HZ. Alternating C.D. 0.5 A/dc^2

The effect of A.C. on electrodeposition of the alloy in presence of chloride ions has been studied by connecting A.C. generator between the working cathode and two platinum wires dipped in the solution as secondary electrodes. A suitable capacitance was used for D.C filtration in the A.C. circuit and a coil used for A.C. filtration in the D.C. circuit. The electroplating process was continued for 45 minutes at 30°C.

A special cell (fig.1) with one anode and several cathodes at different distances from the anode was used for measurement of the throwing power of the electrolytes.

The cathode used in this work consisted of five parts exactly equal in surface area and made an angle of 60° with the anode surface as shown in fig.1.

Every part of the cathode was weighed before and after the deposition. Then the weight of the first cathode (the most close to the anode) was considered as unity, and all the other weights are referred to it.

The temperature - kinetic method[3] was applied for determining the effective energy of activation for electrodeposition process.

$$\text{Log } i = \frac{-E}{2.303\,RT} + K$$

Where i is the value of current at constant polarization potential and at the given temperature T.

The plot of log i vs 1/T gave a straight line of a slope equal to -E/2.303 R.

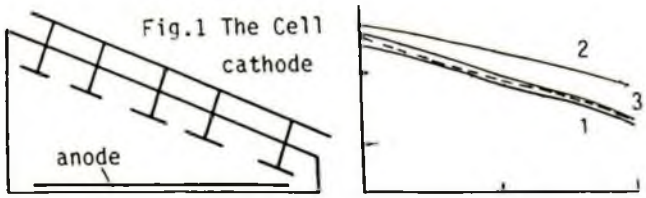


Fig. 2 Throwing power of copper baths
1. $CuSO_4 5H_2O$ (0.1M) + Acetic Acid (1M)
2. 1 + NH_4OH (0.8M)
3. 1 + 0.0013 M S.A.S.
4. 2 + 0.0013 M S.A.S.

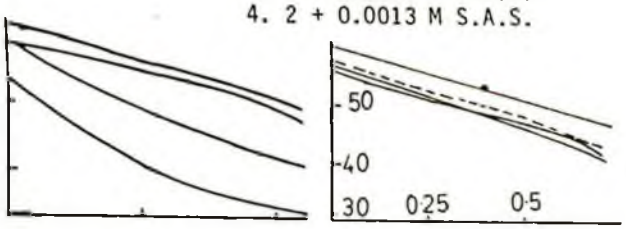


Fig. 3 The throwing power of cadmium baths.
1. $LdSO_4 B/3\ H_2O(0.2M)$ + Acetic Acid (1M)
2. 1 + NH_4OH (0.8M)
3. 1 + 0.0013 M S.A.S.
4. 2 + 0.0013 M S.A.S.

Fig. 4 The throwing power of Cu-Cd alloy baths.
1. $CuSO_4\ 5H_2O$ (0.1M) + $CdSO_4$ 8/3 H_2O (0.25M) Acetic Acid (1M)
2. 1 + NH_4OH (0.8 M)
3. 1 + 0.0013M S.A.S.
4. 2 + 0.0013 M S.A.S.

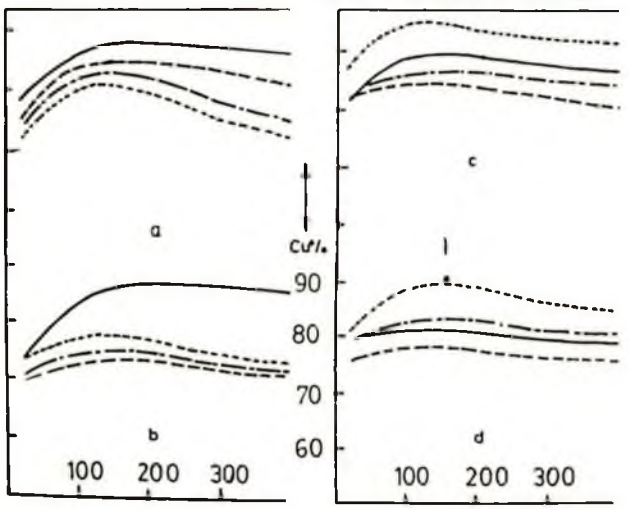


Fig. 5 The effect of superimposition of AC on the composition of deposited alloy

Medium for 5a- $CuSO_4 5H_2O$ (0.1M) $CdSO_4$ 8/3 H_2O 0.25M, acetic acid 1M acetic acid-ammonium 0.8M

Medium for 5b- $CuSO_4\ 5H_2O$ (0.1M), $CdSO_4$ 8/3 H_2O 0.25M, acetic acid-1 M acetic acid-ammonia 0.8M

Medium for 5c- $CuSO_4\ 5H_2O$ (0.1M), $CdSO_4$ 8/3 H_2O 0.25M, acetic acid 1M + 0.0013M SAS

Medium for 5d- $CuSO_4\ 5H_2O$ (0.1M), $CdSO_4$8/3 H_2O 0.25M, acetic acid 1M + NH_4OH 0.8 M 0.0013M SAS

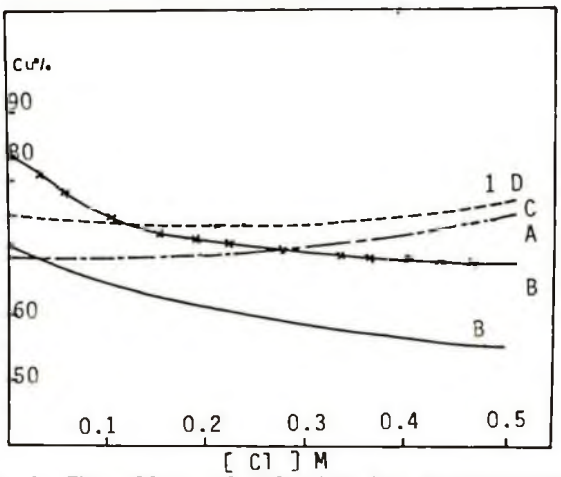


Fig. 6 The effect of chloride ion concentration on the composition of the alloy.

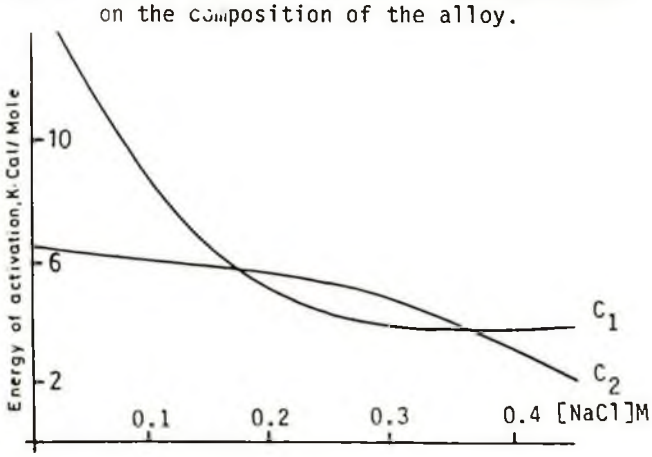


Fig. 7 The effect of Chloride ion on the effective energy of activation
C_1 $CuSO_4$ (0.1N + Acetic acid, IN + S.A.S.
C_2 $CdSO_4$,0.5N + Acetic acid, IN + S.A.S.

RESULTS AND DISCUSSION

Electrodeposition of Cu-Cd alloys was studied to observe quality (color, appearance and presence of dendrites) of the deposit, composition of the alloy and throwing power of the electrolytes.

(i) QUALITY OF THE DEPOSIT :

The effect of chloride ions on the quality of the deposits of copper, cadmium and copper-cadmium alloys has been that copper deposits are slightly

affected by the addition of chloride ions. On the other hand, cadmium deposits are largely affected. This is so because the depolarization effect of chloride ions on cadmium deposition is more than in the case of copper deposition. It was also noticed that the addition of chloride ions to the bath for the deposition of Cu-Cd alloys affects the quality of the deposited alloy to a degree less than noticed in cadmium deposition and more than that of copper deposition. Increase of chloride ion content in the bath is also accompained by the formation of a dark and coarser grained deposits in case of Cd and Cu-Cd alloy than that observed in copper deposits.

The study showed also at low frequencies of A.C. ($\leq$150 H), the small dendrites observed on the edges of the cathode in the alloy deposition disappeared and the deposits became smoother but darker. On the other hand high frequencies (more than 150Hz) of A.C. had no effect.

(ii) Throwing power of Electrolytes:

Representative curves for the distribution of Cu,Cd and Cu-Cd alloy deposits on the different parts of the angular cathodes are shown in Figs.2, 3 and 4. It is quite clear from these figures that the effect of chloride ions on the throwing power decreases in the sequences: cadmium bath $>$ copper-cadmium bath $>$ copper bath. This is so because depolarization effect of chloride ions on cadmium deposition is stronger than an alloy or copper deposition. It was also noticed that the decrease in the throwing power of electrolytes containing surface active substances (sodium salt of β-napthalene acetate) is lower in cadmium bath than in case of coper or alloy deposition from the similar baths. This may be ascribed to the stronger effect of the anionic surface active substances on cadmium deposition than on copper deposition. This in turn must lead to a weakening of the effect of chloride ions (as depolarizer) on the discahrge of cadmium ions, whereas the copper ions discharge remains almost constant.

In general, it could be concluded that, addition of chloride ions decreases the throwing power of all studied electrolytes, but in different ways depending on the presence of anionic S.A.S. and the zero charge point of the electrodeposited metal.

The effect of alternating current on the composition of the alloy deposited is shown in figs. 5a,b,c and d.It is quite clear from these figures that the throwing power of all the electrolytes increases with frequency of the applied A.C. till about 250 Hz and above that it decreases slightly. It seems that this phenomenon is related to the leveling effect of the alternating current, and is attributed to the oscillation of the deposition current between zero and a certain maximum value. Thus the deposition process starts always from zero current at every cycle. The first deposited layer always possesses a very high coating power.

At high frequencies, the throwing power decreases as a result of the diminishing of the alternating current effect.

(iii) The composition of the alloy:

The effect of alternating current on the composition of the alloy is illustrated in fig 5. From the curves shown in these figures, it is quite clear that, the application of A.C. is accompanied by a parallel decrease in cadmium content of the alloy. However, as the frequency of the applied A.C. increases above 150 Hz, the cadmium content in the alloy starts to increase. This indicates that the effect of A.C. oscillation disappears above 150 Hz.

The variation of the alloy composition in the presence of chloride ions illustrates clearly the depolarization effect of this ion. Figure 6 shows the relation between the composition of the alloy and chloride ion concentration in the bath, and indicates that increasing chloride ion concentration (from 0.1 to 0.5 M), the cadmium content increases but at a lower rate (electrolyte A). The increase of cadmium content in the alloy upon increasing chloride ion concentration can be attributed to the higher depolarazation effect of this ion on the deposition of cadmium than on copper deposition[4]. On the other hand, for electrolyte B, the cadmium content of the alloy increases on increasing chloride ion concentration as shown in fig.6.

It is also clear that the increase of chloride ion concentration in bath C which does not contain NH_4OH and in the presence of anionic S.A.S., the cadmium content does not increase as in the absence of the anionic S.A.S., but decreases slightly at chloride ion concentrations more than 0.1 M. This behaviour is quite clear from the relation between the effective energies of activation and chloride ion concentration shown in figure 7.

For electrolyte D, in presence of 0.8 M NH_4OH and S.A.S of anionic character, the decrease of cadmium content in the alloy as a result of increasing chloride ion concentration is smaller.

Generally, the effect of chloride ion on the composition of the alloy in presence of S.A.S of anionic character differs completely from that in the absence of this S.A.S. This behaviour can be attributed to the adsorption of surface active

anions on the cadmium surface during deposition inhibiting to some extent the deposition of cadmium and favouring the discharge of copper ions.

REFERENCES

1. A.T. Vagramyan, A.A. Soutagina, Izv. Akad. Nauk.S.S.S.R 3 (1952) 1910
V.I. Meilk-Gaikazin, P.I.Dolin "New methods in Physicochemical studies" Akad, Nauk SSSR (1950) 115

2. A.N. Sisov, Tr. Kharkav. Institute of Technology, 1.1 (1952). 73.

3. A.I. Vogel (A text book of quantitative inorganic analysis) Third Edition ELBS (1978) p358, 494, 498.

4. L.M. Issa, F.M. El-Cheikh and K.K. Kassem, Revue Roumoaine de Chemie, 24, 403-406 (1979).