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The effect of superimposed a.c. on d.c. on the electrodeposition of Cu–Zn alloys

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The effect of superimposing a sinusoidal alternating current on a direct current on the electrodeposition of Cu, Zn, and Cu–Zn alloys from alkaline tartrate baths is investigated. The data reveal that superimposing a.c. on d.c. decreases the cathodic polarization in all cases. Such results could be attributed to the asymmetric polarizability of the electrode as well as to the concentration changes at the electrode surface. The cathodic efficiency of the parent metals increases with a.c. The zinc content of the alloys decreases with a.c. The effect of a.c. is diminished with increasing either the density of d.c. or the frequency of a.c. in the system.

1. Introduction

Alternating current has a significant effect on many electrode processes. The change of cathodic and anodic potentials depends on the density and frequency of the alternating current. Such an effect of alternating current is considered to be due to the asymmetric polarizability of the electrode [1–5].

The effect of superimposed a.c. on the electrodeposition of single metals has been extensively studied [6–11]. However, little attention has been given to such an effect on the electrodeposition of alloys. Kovac [12] reported that the composition of an alloy may be varied by varying the amplitude and frequency of a.c.

Continuing our investigation on the effect of some plating variables on electrodeposition of alloys, we have investigated the effect of alternating current on the electrodeposition of Cu–Zn alloys from alkaline tartrate bath.

2. Experimental

The electrical circuit used is shown in Fig. 1. The cell consisted of two compartments separated by a sintered glass disc. A Pt sheet cathode, k, (1·6 cm^2), was placed in the cathode compartment, and a Pt wire anode, a, was placed in the anode compartment.

Direct current was supplied by a 6 V battery, T, and introduced into the cell via a variable resistance, R, a choke, H, (2·5 H), and ammeter, A_1. A sinusoidal alternating current was supplied by a signal generator, G, (Audio Frequency Oscillator Type TR-0101) and passed through the cell via a capacitor, C, (100 μF), and ammeter, A_2. The capacitor and the choke were used to separate the circuits of the direct and alternating current.

The cathodic potentials were measured relative to a saturated calomel electrode, s, through a bridge filled with solution under test to avoid

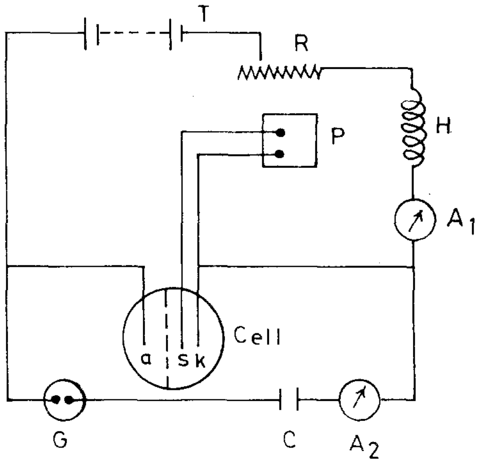

Fig. 1. Electrical circuit for electrodeposition under the effect of d.c. and a.c.

contamination. The potential was recorded using a potentiometer, P, (Radiometer PHM 62).

Alkaline tartrate baths were chosen for the deposition of Cu, Zn, and Cu–Zn alloys. The copper bath had the following composition: 0·3 M $CuSO_4$, 0·7 M Na–K tartrate, 2·5 M NaOH. The zinc bath had the following composition: 0·2 M $ZnSO_4$, 0·7 M Na–K tartrate, 2·5 M NaOH. Two baths were used for alloy deposition, Bath 1 contained 0·3 M $CuSO_4$, 0·2 M $ZnSO_4$, 0·7 M Na–K tartrate, 2·5 M NaOH. Bath 2 contained 0·2 M $CuSO_4$, 0·2 M $ZnSO_4$, 1·2 M Na–K tartrate, 2·5 M NaOH. In all these solutions the pH was 12·90 ± 0·15.

All solutions were made from Analar chemicals using distilled water. 200 ml of fresh solution and clean electrodes were used in each run. Experiments were performed at 25 ± 0·5° C. The plating time was 20 min. Each run was repeated at least twice. The alloy deposit was stripped from the cathode with 1 : 1 dilute nitric acid and subsequently analysed to ascertain the copper and zinc content of the deposit [13].

3. Results and discussion

The effect of sinusoidal a.c. of variable density and constant frequency (f = 50 Hz) superimposed on d.c. on the potentials of the individual copper and zinc deposition is shown in Fig. 2. In general, the polarization curves increase with increasing $i_{d.c.}$ density. Concentration polarization is prominent in these solutions of complex ions. In these solutions, copper is predominantly present as the $[Cu(OH)_2C_4H_4O_6]^{2-}$ complex ion [14], and zinc as the $Zn(OH)_3^-$ zincate ion [15].

Superimposing a.c. on d.c. shifts the polarization of the parent metals in the less negative direction. The effect of a.c. is more pronounced in the case of copper than in the case of zinc especially at low $i_{d.c.}$ densities. Such an effect of a.c. may be due to the fact that the electrode can be considered as an electrically non-linear element [4–6, 16]. Therefore, the sine wave of the a.c. suffers distortion at the electrode surface. In turn, the average value of the electrode potential fluctuates periodically and differs from the potential corresponding to d.c. alone. Moreover, the shift in cathodic polarization may be related to the concentration changes at the electrode surface. Passage of a.c. through a solution of complex ions may produce periodic concentration changes [12, 16]. Vetter [17] gave the concentration changes as the difference of ohmic and capacitive components of the electrolyte, both of which are dependent on the angular frequency of a.c. and

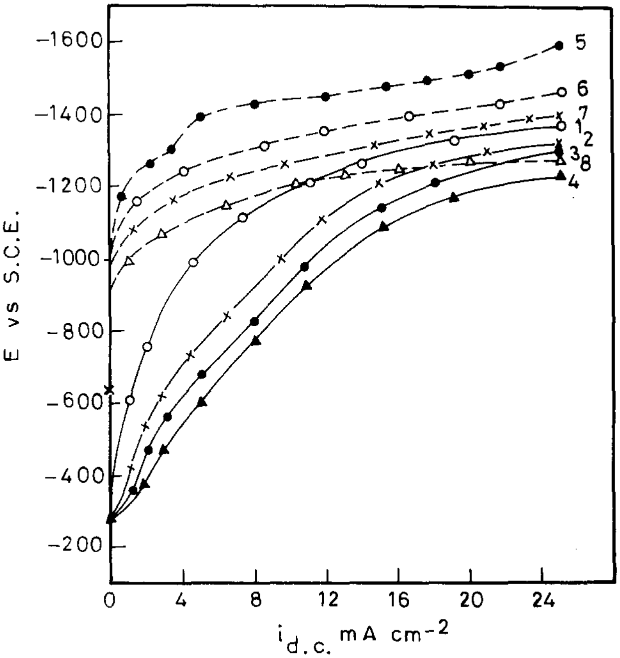

Fig. 2. Effect of a.c. (f = 50 Hz) on cathodic potential. Curves 1–4 for Cu, Curves 5–8 for Zn. (1) $i_{a.c.} = 0$; (2) $i_{a.c.} = 5$ mA cm^{-2}; (3) $i_{a.c.} = 10$ mA cm^{-2}; (4) $i_{a.c.} = 20$ mA cm^{-2}; (5) $i_{a.c.} = 0$; (6) $i_{a.c.} = 5$ mA cm^{-2}; (7) $i_{a.c.} = 10$ mA cm^{-2}; (8) $i_{a.c.} = 20$ mA cm^{-2}.

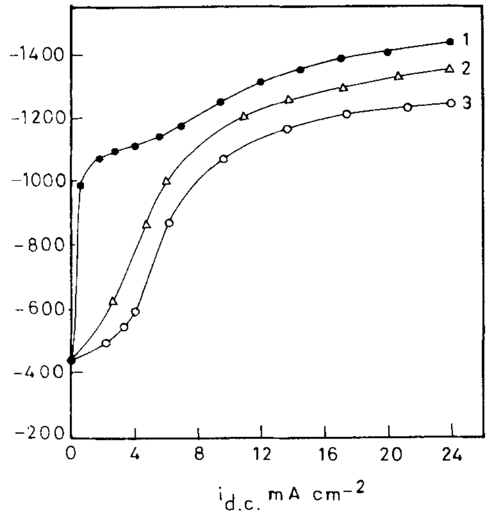

Fig. 3. Effect of a.c. ($f = 50$ Hz) on cathodic potential of Cu–Zn alloy in Bath 1. (1) $i_{a.c.} = 0$; (2) $i_{a.c.} = 5$ mA cm^{-2}; (3) $i_{a.c.} = 10$ mA cm^{-2}.

the reaction rate constant. The concentration wavelength as well as penetration depth are also dependent on the same parameters.

Figs. 3 and 4 show the effect of a.c. on the polarization curves for the deposition of Cu–Zn alloy from Baths 1 and 2, respectively. The data reveal that superimposing a.c. on d.c. also shifts the potential of alloy deposition in the less negative direction. The effect of a.c. is more dominant at low $i_{d.c.}$. Moreover, the data of Fig. 4 show that with increasing a.c. frequency, the effect of a.c. decreases. Qualitatively, however, one would expect that at a higher frequency, the periodic fluctuation of the potential would not be able to follow the fast change in current. In addition the penetration depth of the concentration waves of the reactants becomes smaller [12].

Fig. 5 illustrates the influence of a.c. of constant frequency ($f = 50$ Hz) on cathodic efficiency for copper and zinc deposition. The efficiency of copper deposition is above 100% at lower $i_{d.c.}$ densities. This may be due to the deposition of copper (I) oxide which subsequently can be incorporated into the deposit [18]. Superimposing a.c. on d.c. enhances the efficiency of copper deposition; the greater the $i_{a.c.}$, the higher the efficiency, specially at lower $i_{d.c.}$. This is because as the a.c. increases, the electrode spends more time in the anodic cycle of a.c. and this may be reflected in the formation of more oxides, thus resulting in higher efficiency. With increasing $i_{d.c.}$, more material is required according to Faraday's law therefore the effect of d.c. becomes more pronounced.

With respect to zinc deposition, the efficiency increases with increasing both $i_{d.c.}$ and $i_{a.c.}$. Here also the effect of a.c. decreases with increasing $i_{d.c.}$. Under similar conditions the efficiency-

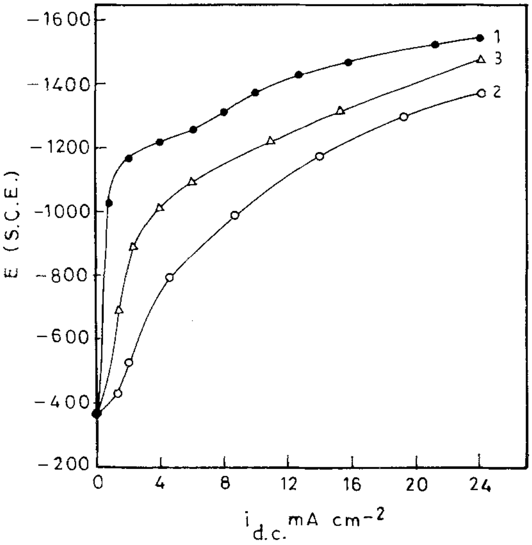

Fig. 4. Effect of a.c. on cathodic potential of Cu–Zn alloy in Bath 2. (1) $i_{a.c.} = 0$; (2) $i_{a.c.} = 10$ mA cm^{-2}, $f = 50$ Hz; (3) $i_{a.c.} = 10$ mA cm^{-2}, $f = 1000$ Hz.

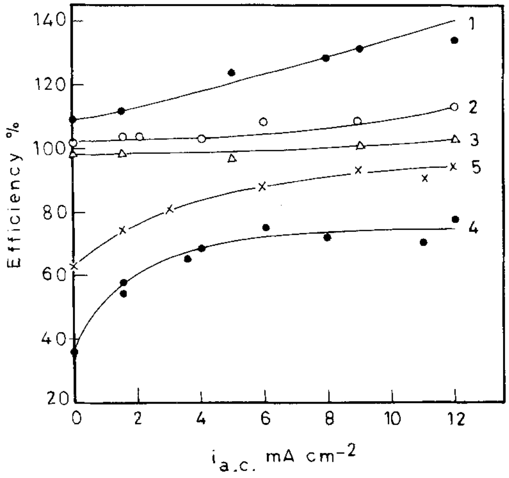

Fig. 5. Effect of a.c. ($f = 50$ Hz) on the individual cathodic efficiency. Curves 1–3 for Cu, Curves 4 and 5 for Zn. (1) $i_{d.c.} = 5$ mA cm^{-2}; (2) $i_{d.c.} = 10$ mA cm^{-2}; (3) $i_{d.c.} = 20$ mA cm^{-2}; (4) $i_{d.c.} = 10$ mA cm^{-2}; (5) $i_{d.c.} = 20$ mA cm^{-2}.

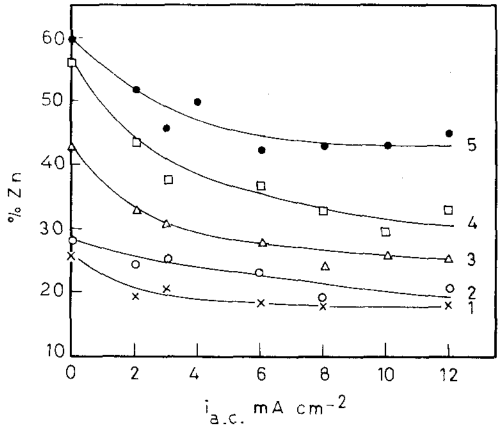

Fig. 6. Effect of a.c. ($f = 50$ Hz) on the percentage of Zn in alloy. Curves 1–3 in Bath 1, Curves 4 and 5 in Bath 2. (1) $i_{d.c.} = 7$ mA cm^{-2}; (2) $i_{d.c.} = 10$ mA cm^{-2}; (3) $i_{d.c.} = 20$ mA cm^{-2}; (4) $i_{d.c.} = 10$ mA cm^{-2}; (5) $i_{d.c.} = 20$ mA cm^{-2}.

increasing effect of a.c. is somewhat more on zinc than on copper deposition.

The effect of superimposed a.c. of variable density and constant frequency ($f = 50$ Hz) on the composition of the Cu–Zn deposits from Baths 1 and 2 is given in Fig. 6. The zinc content (the less noble metal) of the deposit increases with increasing $i_{d.c.}$. This behaviour is characteristic of a regular alloy plating system [19].

By superimposing a.c. on d.c., the percentage of zinc in the deposit decreases at first and then levels off as $i_{a.c.}$ increases. Such behaviour is difficult to explain on the basis of the effect of a.c. on the efficiency of single copper and zinc deposition from their individual baths.The variation in the composition of the deposit may be attended by shifts of the deposition potentials of the parent metals under the effect of a.c. The shift of the potential of copper deposition to the more positive value is somewhat greater than that for zinc (Fig. 2), therefore this effect increases the interval of potential between them and hence a decrease in the percentage of zinc in the deposit should result.

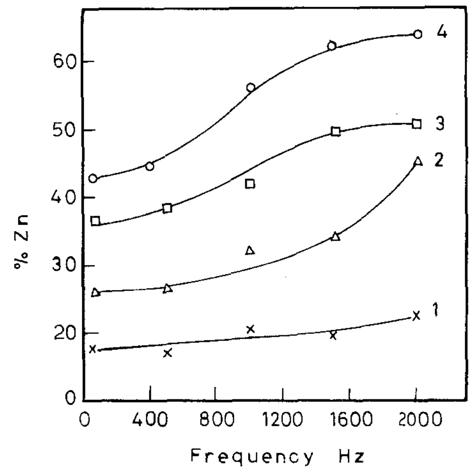

Fig. 7. Effect of a.c. frequency on the percentage of Zn in alloy. Curves 1 and 2 in Bath 1, Curves 3 and 4 in Bath 2. (1) $i_{d.c.} = 7, i_{a.c.} = 6$ mA cm^{-2}; (2) $i_{d.c.} = 20, i_{a.c.} = 10$ mA cm^{-2}; (3) $i_{d.c.} = 10, i_{a.c.} = 6$ mA cm^{-2}; (4) $i_{d.c.} = 20, i_{a.c.} = 10$ mA cm^{-2}.

Some experiments were carried out to examine the effect of frequency on the composition of the deposited alloy. Fig. 7 shows the percentage of zinc as a function of frequency from the two baths for conditions of constant $i_{d.c.}$ and $i_{a.c.}$. In all cases, the percentage of zinc decreases, approaching d.c. values at high frequencies, where the contribution from the a.c. component becomes negligible.

Superimposing a.c. gives smooth and bright deposits. The colour of the deposit changes from yellow to red with $i_{a.c.}$.

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