

Electroplating of a Co–Cu alloy from a citrate bath containing boric acid

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Abstract: The effects of bath composition, current density and temperature on cathodic polarization, cathodic current efficiency of codeposition, composition and structure of Co–Cu alloys electroplated on a steel substrate from citrate baths have been studied. Addition of boric acid to citrate electrolyte increases the percentage of Co in the deposits and improves the quality of these deposits. The cathodic current efficiency of the baths is relatively high and increases with increases in the metal content in the bath and the current density but decreases with temperature. The composition of the deposit is controlled by the applied current density. At low current densities, Cu-rich alloys were obtained. At higher current densities, the composition of the alloys was controlled by the limiting current density of Cu codeposition. The Co content of the deposits increases with increases in the metal content in the bath and the temperature. The structure of the deposited alloys was characterized by anodic stripping and X-ray diffraction techniques. The deposited alloys consisted of a single solid solution phase with a face-centred cubic structure.

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Keywords: Co–Cu alloys; electrodeposition; citrate bath; boric acid

INTRODUCTION

The electrodeposition of Co–Cu alloys is of great interest because they are frequently used in a variety of industrial applications. Co–Cu alloys with high cobalt content can be used for catalytic purposes.^{1,2} Like Ni–Cu alloys, they are characterized by high corrosion resistance.^{3,4} In recent years, Co–Cu alloys have been widely applied as a non-magnetic material or electric resistance device.⁵

Electroplating of Co–Cu alloys has been studied by several authors and the processes were reviewed by Brenner.⁶ Fink and Hotton⁷ electrodeposited Cu–Co from a simple bath containing copper sulfate and cobalt sulfate. The deposits were a gross admixture of the two metals. Several complexing agents have been tested in an attempt to improve the quality of the deposits, but the most interesting seems to be the citrate bath⁴ because it can be used to electrodeposit good quality deposit at high current efficiency. Citrate electrolytes are particularly attractive because of their inherent low toxicity. Moreover, citrate can function as a brightening⁸ and levelling agent⁹ thus eliminating the need for other bath additives.

Boric acid has been of interest in the electroplating of Ni,¹⁰ Ni–Zn alloys¹¹ and Co–Zn alloys.¹² It is now believed that boric acid either complexes with Ni and Co ions, acting as a homogeneous catalyst or adsorbs on the electrode surface, thus affecting the resulting

morphology and compositional characteristics. It has been found that, in Co–Zn deposition, boric acid raised the Co content in the alloy and increased the nucleation density of the deposit.¹² However, the influence of boric acid on the electrodeposition of Co–Cu alloys has not, as yet, been the subject of investigation. Therefore, the role of boric acid on Co–Cu electrodeposition is of interest.

The subject of the present study is the electrodeposition of Co–Cu alloys from citrate baths containing boric acid. The advantages of these baths are not only their cheapness but also their non-polluting effect on the environment. The influences of bath constituent and some operating factors on cathodic polarization, cathodic current efficiency and composition and quality of the deposits were investigated.

EXPERIMENTAL

Experiments were carried out in baths containing copper sulfate (CuSO₄), cobalt sulfate (CoSO₄), sodium sulfate (Na₂SO₄), sodium citrate (Na₃C₆H₅O₇) and boric acid (H₃BO₃). All solutions used were freshly prepared with doubly distilled water and analytical grade chemicals. The pH of each solution was measured using a pH-meter (CG 803 Scott Gerate). The composition and pH value of each solution used are given in Table 1.

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Table 1. Composition of some baths used

Bath number	[CoSO ₄] mol dm ⁻³	[CuSO ₄] mol dm ⁻³	[Na ₂ SO ₄] mol dm ⁻³	[Na ₃ C ₆ H ₅ O ₇] mol dm ⁻³	[H ₃ BO ₃] mol dm ⁻³	pH
1	0.036	–	0.07	0.31	0.32	7.20
2	–	0.16	0.07	0.31	0.32	4.90
3	0.036	0.16	0.07	–	–	4.10
4	0.036	0.16	0.07	0.31	–	4.57
5	0.036	0.16	0.07	0.31	0.32	4.63

The experimental set-up used consisted of a rectangular Perspex cell equipped with a plane hot-rolled mild steel cathode of composition C 0.4%–Si 0.2%–Mn 0.26%–S 0.015%–P 0.014%–Al 0.08%–Ni 0.014% (locally produced by the Egyptian Iron and Steel Company), and a platinum sheet anode. Each electrode had the dimensions 2.5 × 3 cm and the cathode was mechanically polished with 000 mesh emery paper, washed with distilled water, ethanol and weighed. The experiments were conducted at the required temperatures (± 1 °C) with the help of an air thermostat. The plating duration was 30 min, after which the cathode was withdrawn, washed with water, ethanol, dried and weighed. The alloy compositions were determined using atomic absorption spectrophotometry (AAS) (Perkin–Elmer) after dissolving the deposited alloy by digestion in concentrated hydrochloric acid and making up the solution obtained with distilled water to 100 cm³.

The galvanostatic cathodic polarization measurements were conducted in a three-electrode cell provided with a steel cathode rod of the same composition as mentioned above. The working steel rod cathode was embedded in Araldite so that a cross-sectional area of 0.64 cm² was in contact with the solution. A platinum wire (2 cm length and 0.15 cm diameter) was used as the counter electrode. A saturated calomel electrode (SCE) was used as a reference electrode to which all potentials are referred. The latter was connected to the cell with a Luggin capillary filled with the solution under test to minimize contamination. The capillary tip of the bridge was pressed against the working electrode to minimize the *i*-*R* drop.

The potential of the working electrode was measured using potentiometer (Welch, Scientific Co, Shokie, USA; 120 V/60 HZ). The anodic stripping voltammetry measurements were made in the previously mentioned three-electrode cell, where the working electrode was a glassy carbon disk of area 0.5 cm², the counter electrode was a platinum wire together with a saturated calomel electrode (SCE). These were connected to a potentiostat, model 273, and X–Y recorder, model RE 0091.

The phase and crystal structure of the ‘as-deposited’ binary alloy films obtained from selected solutions were investigated using a Philips PW 1390 X-ray diffractometer at 40 kV and 20 mA. The surface morphology of the deposits was studied using SEM

by means of a Joel microscope (model DSM-5400 LV).

RESULTS AND DISCUSSION

Cathodic polarization

To elucidate the role of sodium citrate and boric acid on the electrodeposition of Co–Cu alloys, the effects of these two compounds on cathodic polarization during the codeposition process were determined. Figure 1 (curve a) represents the galvanostatic cathodic polarization in a bath containing CoSO₄, CuSO₄ and Na₂SO₄ (bath 3). It is observed that the polarization curve is steep and shows little overpotential. Codeposition under such conditions may take place via kinetic control. The addition of citrate ions to the above solution involves drastic changes in the cathodic polarization (curve b). It is known that in the presence of cit³⁻ (cit³⁻ is C₆H₅O₇³⁻) ions, both Co²⁺ and Cu²⁺ form a series of soluble complex species.^{13,14} According to the literature^{14,15} the most predominant complex species in the bulk solution are Co cit⁻ and Cu cit⁻ in addition to the uncomplexed Co²⁺ and Cu²⁺ species. Therefore, the alloy could be obtained by electroreduction of either the complexed and

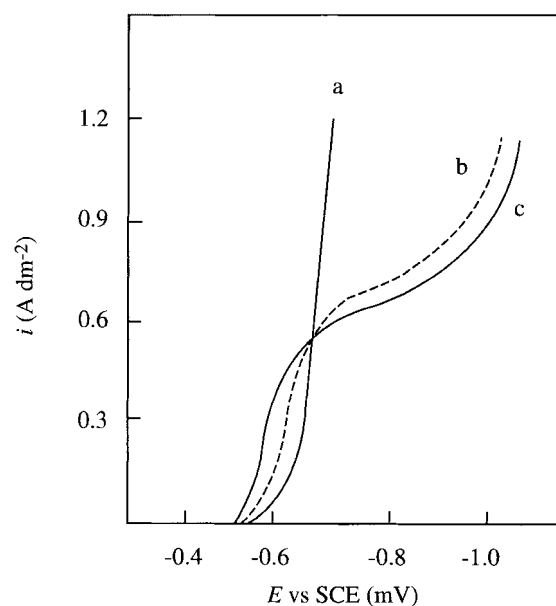
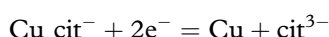
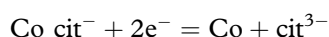
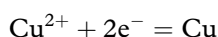
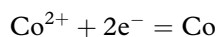


Figure 1. Galvanostatic polarization curves for Co–Cu alloy at 25 °C; (a) from bath 3; (b) from bath 4; (c) from bath 5.

uncomplexed species simultaneously¹⁵ as follows:



The relative abundance of each species in solution depends upon the prevailing conditions. Inspection of curve b of Fig 1 reveals that at less negative potentials (<–630 mV), the presence of citrate ions has no significant influence on cathodic polarization. At larger negative potentials, the polarization curve exhibits a limiting current plateau. At potentials more negative than –970 mV, the current density starts to increase again. It is worth noting that the addition of boric acid to the above citrate bath increases the cathodic polarization and strongly reduces the limiting current density (curve c). This behaviour comes about by the formation of complexes between Cu^{2+} ions and boric acid.¹⁴ In this case the concentrations of the uncomplexed Cu^{2+} ions decrease.

Figure 2 shows the cathodic polarization curves of pure Co (curve a), pure Cu (curve b) and Co–Cu alloy (curve c) in baths containing citrate and boric acid under similar conditions. It is clear that the cathodic polarization curve of the alloy is similar to that of pure Cu, each exhibiting a limiting current plateau. These results imply that under the limiting conditions, the codeposition process is controlled by diffusion of Cu. It seems that the concentrations of complexed and uncomplexed Cu^{2+} ions are extremely small at the electrode surface while the concentrations of Co species remain close to their bulk values. Podlaha *et*

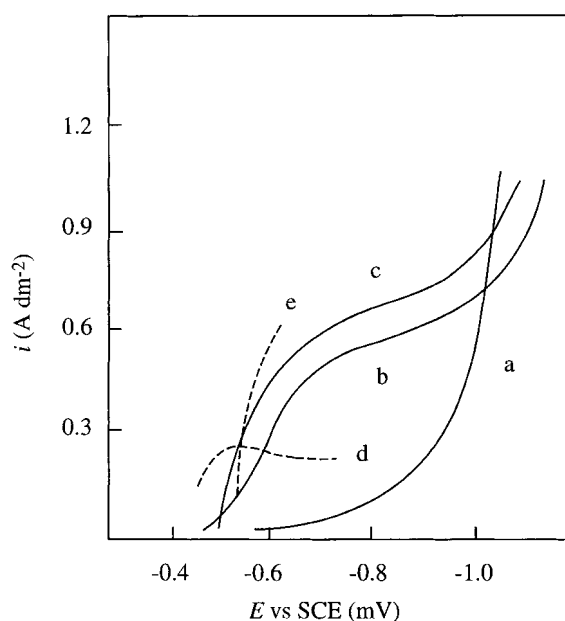


Figure 2. Galvanostatic polarization curves at 25°C for pure Co from bath 1 (curve a), pure Cu from bath 2 (curve b), Co–Cu alloy from bath 5 (curve c). The dotted curves represent the partial current density for Cu (curve d) and Co (curve e) from bath 5.

*al*¹⁵ reported that Cu codeposition under limiting conditions is almost entirely due to the electroreduction of Cu^{2+} ions. Inspection of the data of Fig 2 leads to the conclusion that at less negative potentials (less than –980 mV), the polarization curve of pure Co lies at considerably more negative potentials than of Cu, indicating that Cu is the nobler metal in this system. However, at more negative potentials than this value, the cathodic polarization of pure Co becomes less negative than that of pure Cu, indicating that Co behaves as the nobler metal. Therefore, one can conclude that at the less negative potentials (less than –550 mV), Cu, the more noble metal, deposited preferentially and Cu-rich alloys are expected to form. In this case, codeposition proceeds via kinetic control. On the other hand, at the more negative potentials (less than –550 mV), Co, the more noble, becomes the more depositable metal. It seems that a high negative potentials, boric acid acts as a homogeneous catalyst for the deposition of Co.¹² Under such conditions, codeposition proceeds under Cu diffusion control.

The partial current densities of each metal during codeposition could be calculated from the alloy composition current density curve as recommended by Brenner.⁶ The dotted curves in Fig 2(d and e) represent the partial current densities of Cu and Co codeposition respectively. It is obvious that at potentials less negative than –550 mV, the partial current density of Cu is higher than that of Co. Cu deposition therefore proceeds preferentially to Co deposition. At the more negative potentials, the partial current density of Cu attains a limiting value while the partial current density of Co becomes higher than that of Cu and increases with the applied current density. Since the diffusion limiting current is the maximum current of Cu codeposition in a given bath, the excess of current over the limiting current is consumed by Co deposition.

The effects of metal ion concentrations and temperature on the cathodic polarization of codeposition from the baths containing citrate and boric acid were determined. Figure 3 shows that the cathodic polarization reduced and the limiting current density increased as the Cu content in the bath increased. The same behaviour was observed as the Co content in the bath increased (Fig 4). The latter unusual trend could be explained on the basis that Co^{2+} may take some of the complexing agents. The Cu^{2+} ions, therefore, become less tightly complexed and the relative concentration of the uncomplexed Cu^{2+} increases. This decomplexing of Cu more than compensated for the effect of the increase in the concentration of Co in the bath. Figure 5 shows the influence of temperature on cathodic polarization curves of codeposition. Raising the temperature decreases the limiting current density of Cu codeposition.

Composition of Co–Cu electrodeposited alloy

Figure 6 shows the effects of the addition of boric acid to the citrate bath on cathodic current efficiency

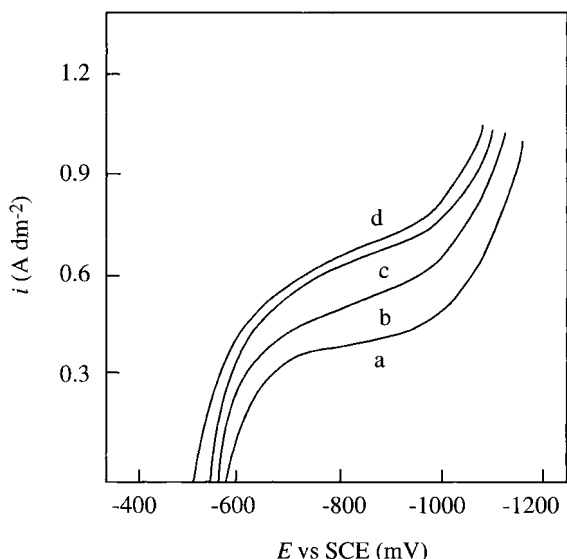


Figure 3. Effect of Cu content in the bath on the cathodic polarization of Co–Cu alloys at 25°C from bath 5 but with different concentrations of CuSO_4 . (a) 0.04M; (b) 0.08M; (c) 0.12M; (d) 0.16M CuSO_4 .

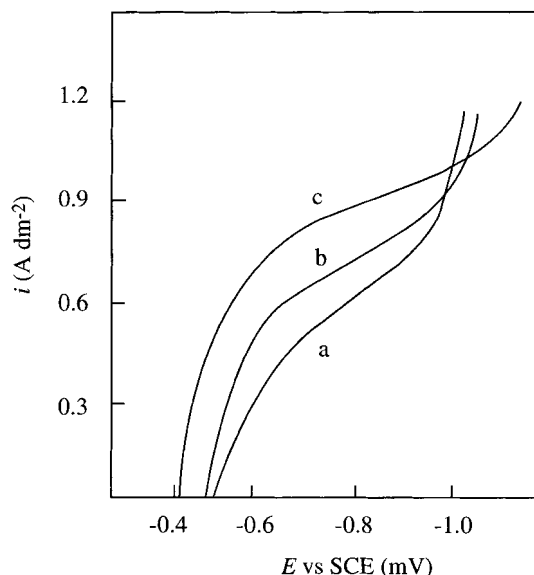


Figure 5. The effect of temperature on cathodic polarization of Co–Cu alloys from bath 5 at (a) 45°C; (b) 25°C; (c) 15°C.

(CCE) and Co content (Co%) in the deposit as a function of current density. The composition reference line (CRL) in these figures represents the percentage of Co in baths. In the case of the boric-free citrate bath (bath 4) the CCE is high (about 100%) and independent of current density. The addition of boric acid decreases the CCE, especially at low current densities. However, in the absence and presence of boric acid, the Co% in the deposit increases with increases in the current density. It is interesting to observe that the curve of Co content in the deposit cut the CRL at a certain transition current density (the current density at which the Co content in the deposit is identical with its percentage in the bath). At current densities lower than the transition current

density, the percentage of Co in the deposits is lower than the CRL, indicating preferential deposition of Cu (the nobler component). However, at current densities higher than the transition one, the percentage of Co in the deposits lies above the CRL, indicating preferential deposition of Co (the more nobler metal under these conditions). This transition state is due to the limitation of Cu codeposition and commencement of Co codeposition with increasing current density. The transition current density is related to the limiting current density of Cu codeposition. Any factor increasing the limiting current density should increase the transition current density. Observation of the data of Fig 6 reveals that the addition of boric acid to citrate baths decreases the transition current density, indicat-

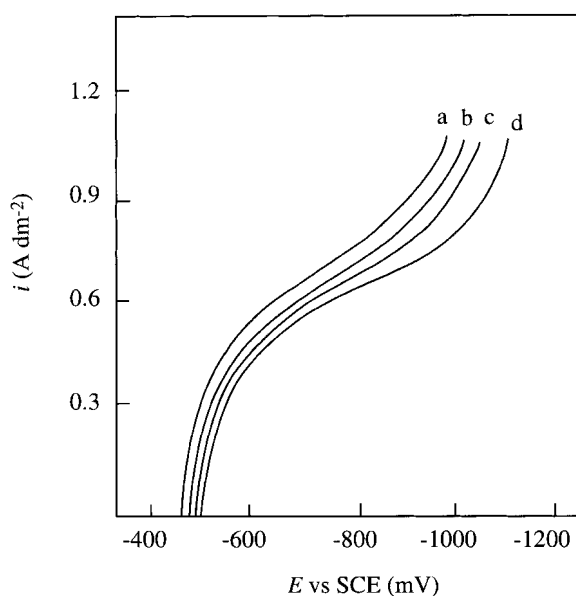


Figure 4. Effect of Co content in the bath on the cathodic polarization of Co–Cu alloys at 25°C from bath 5 but with different concentrations of CoSO_4 . (a) 0.036M; (b) 0.072M; (c) 0.108M; (d) 0.144M CoSO_4 .

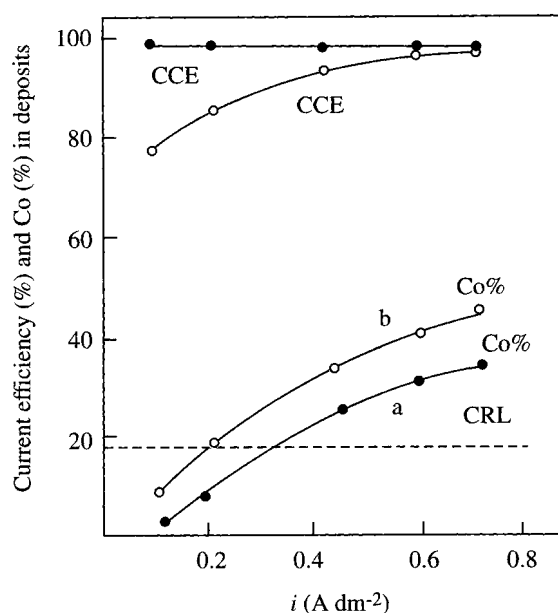


Figure 6. The effect of current density on cathodic current efficiency (CCE) for alloy deposition and on the cobalt percentage (Co%) in the deposit at 25°C; (a) from bath 4; (b) from bath 5.

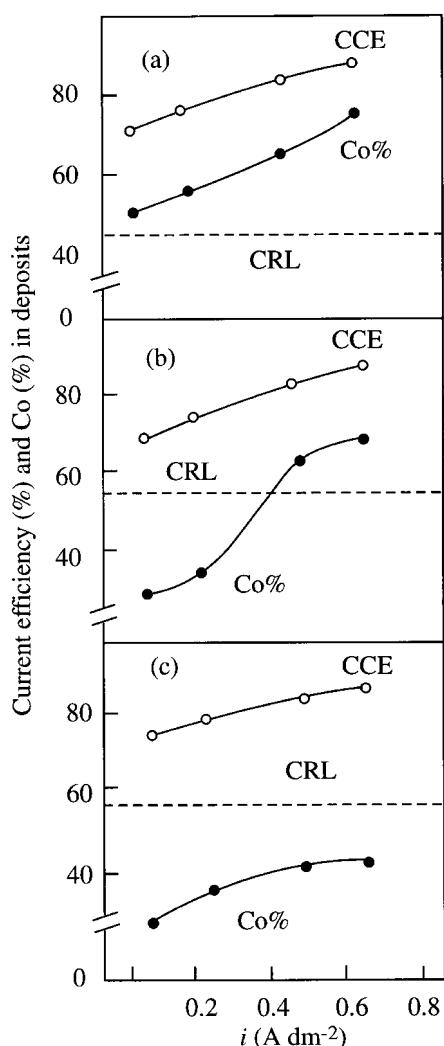


Figure 7. Effect of Co content in the bath on the cathodic current efficiency (CCE) for alloy deposition and on the cobalt percentage (Co%) in the deposit at 25°C from baths containing 0.07M Na_2SO_4 , 0.31M sodium citrate, 0.32M boric acid, 0.063M CuSO_4 and (a) 0.036M; (b) 0.072M; (c) 0.144M CoSO_4 .

ing further acceleration of Co codeposition. These results are in good agreement with cathodic polarization curves.

Figure 7 illustrates the dependency of Co content in the bath on CCE of codeposition and on Co content in the deposit as a function of current density. The CCE increases with increase of both current density and the Co content in the bath. At the lowest Co content in the bath (0.036M CoSO_4), the Co content in the deposit lies above the CRL, indicating preferential deposition of Co over the whole range of current density used (Fig 7(a)). With increases in the Co content in the bath (0.072M CoSO_4), it is seen that there is a transition from a state where Co is the more depositable metal to a state where Cu becomes the preferential depositable metal, as shown in Fig 7(b). It is found that the transition current density increases with increases in the Co content in the bath. At still higher Co contents in the bath (0.144M CoSO_4), the curve of the Co content in the deposits lies below the CRL over the whole range of current density used (Fig 7(c)). By

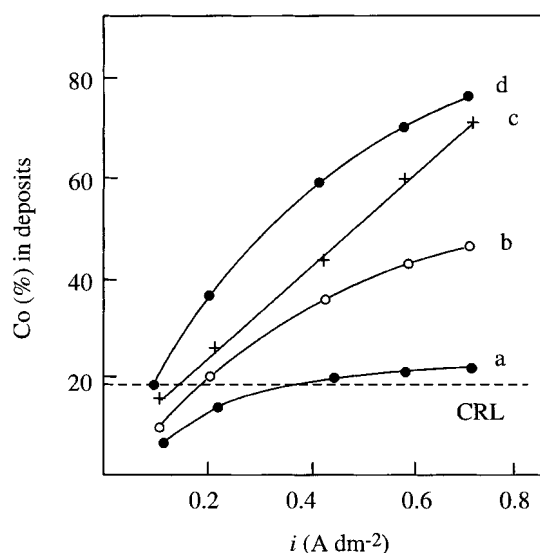


Figure 8. Effect of temperature on the cobalt percentage (Co%) in the deposit from bath 5. (a) 15°C; (b) 25°C; (c) 35°C; (d) 45°C.

comparing the data of Fig 6 (curve b) and Fig 7 (curve a) it is clear that the Co content in the deposits decreases with increases in the Cu content in the bath.

The influence of temperature on Co content in the deposit is shown in Fig 8. The results display that the Co content in deposits increases markedly with increases in the temperature, especially at high current densities. Moreover, the transition current density decreases as the bath temperature is increased. The effect of temperature on the alloy composition is in good agreement with the results of the effect of temperature on cathodic polarization (Fig 5).

Stripping voltammetry

In order to analyse the alloy deposits *in situ*, potentiodynamic anodic stripping was carried out since this method has been shown to be useful in characterization of deposited alloy.¹⁶ A series of voltammetric stripping experiments was performed by deposition of the alloys on glassy carbon electrodes under different plating conditions at constant deposition potential (-1.2V) for constant time (400s). Potentiodynamic anodic stripping was performed immediately in the same solution at a scan rate of 10mV s^{-1} . Figure 9 shows the stripping voltammogram of alloy deposited from bath 5 at 25°C. For comparison, stripping experiments were carried out on deposits of the two pure metals under similar conditions and the results are given in Fig 9. It is obvious that the voltammograms of the alloy and the pure metals have only one dissolution peak. The dissolution peak for pure Cu appears at a more positive potential than that of pure Co. The alloy dissolution peak appears at a more noble potential than those of the peaks associated with Co and Cu components. The existence of the alloy peak at a more noble potential is attributed to either a significant free energy change in mixing, or some kinetic factor which causes the shift of the peak away from its

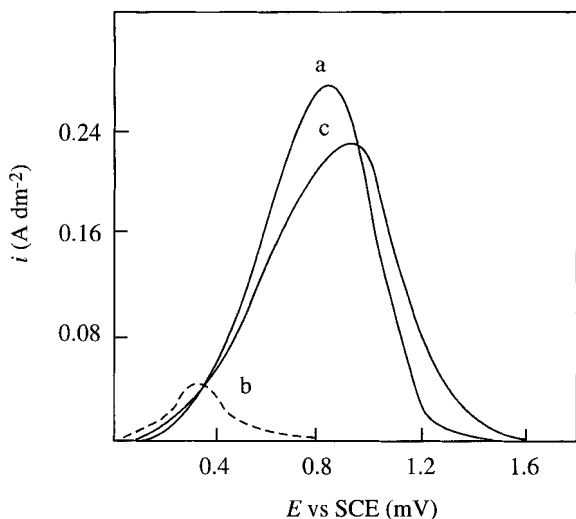


Figure 9. Anodic stripping curves at scan rate 10 mV s^{-1} at 25°C for; (a) pure Cu from bath 2; (b) pure Co from bath 1; (c) Co–Cu alloys from bath 5.

reversible position in the positive direction.¹⁷ The appearance of this single peak indicates that the alloy consists of one phase (solid solution). In this case, the two components (Co and Cu) dissolve simultaneously so that the resulting voltammogram shows only one peak.

Figures 10–12 illustrate the influence of some plating variables on the stripping voltammograms of alloy deposits. The anodic stripping charge (the area under the peak) under the prevailing conditions can be taken as a qualitative measure for the CCE of codeposition.¹⁶ Figures 10 and 11 show that the stripping charge increases with increases in both the Cu and Co content in the bath, indicating that the CCE of codeposition improves with increases in the metal content in the bath. This improvement is related to the increase in the partial current efficiency of Cu deposition, since the chemical analysis shows that the

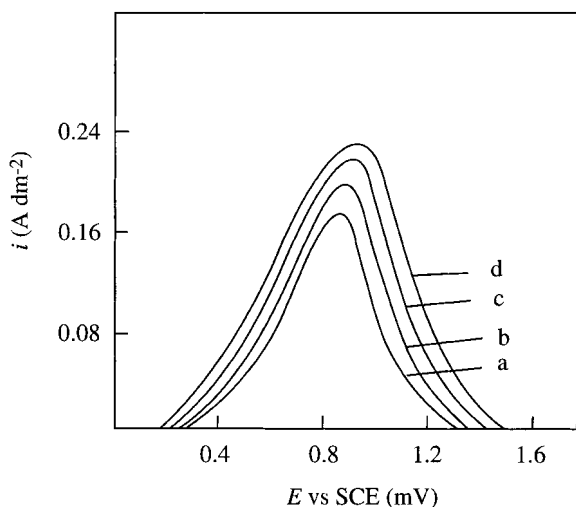


Figure 10. Anodic stripping curves for Co–Cu alloys deposited at 25°C from bath 5 but containing different contents of CuSO_4 ; (a) 0.04 M ; (b) 0.08 M ; (c) 0.12 M ; (d) 0.16 M CuSO_4 .

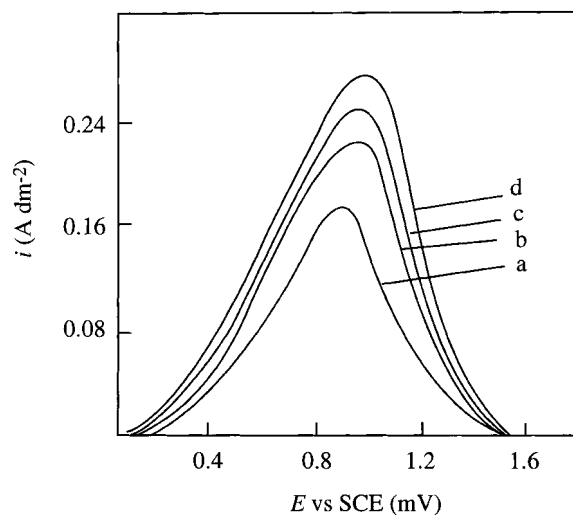


Figure 11. Anodic stripping curves for Co–Cu alloys deposited at 25°C from bath 5 but containing different contents of CoSO_4 ; (a) 0.036 M ; (b) 0.072 M ; (c) 0.108 M ; (d) 0.144 M CoSO_4 .

partial current efficiency of Cu enhances with increases in both the Cu and Co content in the bath. On the other hand, the stripping charge and consequently the CCE of codeposition decreases with increases in the bath temperature, as inferred from the data of Fig 12. This trend could be attributed to the decrease in the partial current efficiency of Cu since the partial current efficiency of Co increases with increasing temperature (Fig 8).

X-ray diffraction

In order to get more information about the phase structure of Co–Cu alloys electrodeposited from bath 5, X-ray diffraction analysis was carried out on some ‘as-deposited’ samples formed at different current densities. The lattice parameters were calculated and some of the results are given in Table 2. Inspection of these data displays the formation of single phase alloys

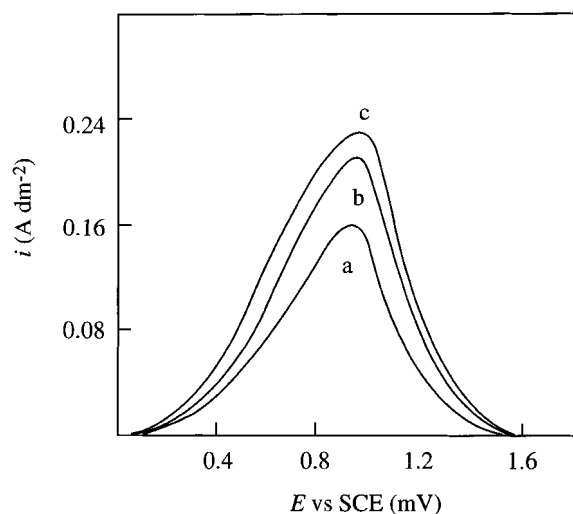


Figure 12. Anodic stripping curves for Co–Cu alloys deposited at 25°C from bath 5, at different temperatures; (a) 45°C ; (b) 35°C ; (c) 25°C .

Table 2. X-ray studies of the alloys deposited from bath 5 at 25 °C and at different current densities. Samples: (1) at $i=0.23\text{A dm}^{-2}$ (2) at $i=0.46\text{A dm}^{-2}$ and (3) at $i=0.70\text{A dm}^{-2}$

Sample	Current density (A dm^{-2})	Alloy composition (%)		Lattice parameters			Lattice
		Co	Cu	2θ	d (nm)	a (nm)	
1	0.23	27	68	43.4	0.2084	0.3608	fcc
2	0.46	49	46	43.4	0.2084	0.3608	fcc
3	0.70	75	25	43.4	0.2083	0.3608	fcc

with face-centred cubic (fcc) structure irrespective of the composition of the alloys. These results are in good agreement with those obtained from stripping analysis, which shows one dissolution peak (single phase) regardless of the composition of the alloys.

Surface morphology

It is observed that in boric acid-free citrate solutions, the deposits were generally semibright and contained coarse grains. Nonetheless, addition of boric acid produced bright and smooth deposits with a metallic lustre. The surface morphologies of the 'as-deposited' Co–Cu alloys were examined by a scanning electron microscope. Some representative SEM micrographs are shown in Fig 13. It is observed that the deposits are generally composed of fine grains. This observation could be attributed to the presence of boric acid in the bath which inhibits the surface mobility of the adatoms, (possibly by adsorption), thereby producing a fine-grained deposit.¹² However, at low current

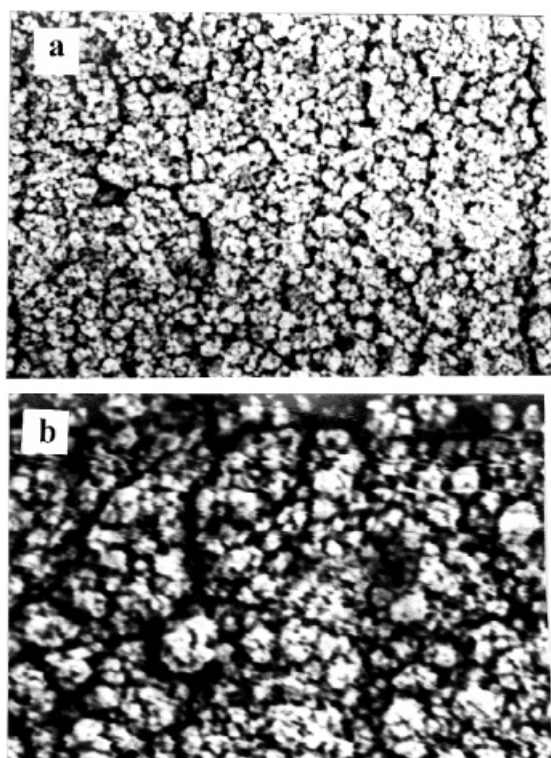


Figure 13. Scanning electron micrographs of Co–Cu alloy electrodeposited on a steel substrate from bath 5 at 25 °C, 30 min and different current densities: (a) $i=0.23\text{A dm}^{-2}$; (b) $i=0.58\text{A dm}^{-2}$ (magnification of 400 \times).

density (0.23A dm^{-2} , Fig 13(a)) the deposited film (10% Cu) consists of finer grains than those produced at higher current density (0.58A dm^{-2}). This increase in the grain size could be due to the increase in Co% in the deposit.¹⁸

CONCLUSIONS

Compact and bright Co–Cu binary alloys were electroplated satisfactorily on steel sheet from baths containing cobalt sulfate, copper sulfate, sodium sulfate, sodium citrate and boric acid ($\text{pH}=4.6\pm 0.2$). The effects of bath composition, current density and temperature on cathodic polarization, cathodic currents efficiency of codeposition, composition and structure of the deposited alloys were investigated. The cathodic current efficiency of the bath was relatively high and improved with increases in the current density and metal content in the bath but decreased with increasing temperature.

The composition of the deposits is strongly dependent upon the applied current density. At low current densities (lower than a certain transition current density), copper, the more noble component, deposited preferentially and Cu-rich alloys were obtained. At high current densities (above the transition current density), cobalt became the nobler metal and was deposited preferentially and Co-rich alloys were obtained. These alloys can be used for catalytic purposes, and to protect steels from corrosion. This transition in the codeposition process is due to the limitation of copper codeposition. The value of the transition current density increases with increase in the metal content in the bath but decreases with increases in the temperature.

The addition of boric acid tends to increase the percentage of cobalt in the deposited alloys.

The deposited alloys formed from the present bath consisted of a single solid solution phase with a face-centred cubic structure irrespective of the composition of the alloys.

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