



# Electrochemistry of the SUCOPLATE<sup>®</sup> electroplating bath for the deposition of Cu–Zn–Sn alloy

## Part II: Influence of the concentration of bath components

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### Abstract

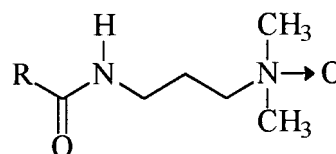
The chemistry of a commercial alkaline cyanide electroplating bath used for the deposition of a Cu–Zn–Sn alloy has been investigated. The voltammetry, the deposit composition and the morphology have been investigated as a function of the concentrations of the three metal ions, Cu(I), Zn(II) and Sn(IV) as well as the concentrations of cyanide, hydroxide, carbonate and ‘Copper Glo’ additive. It is shown that all components combine to control the bath performance although the trends in alloy composition and quality can be predicted from the known chemistry of the bath. It is also concluded that the deposition of tin has an important role in initiating the growth of alloy layers.

### 1. Introduction

The previous paper [1] reported the application of voltammetry and electron microscopy to an investigation of the electrodeposition of a Cu–Zn–Sn alloy from a commercially available alkaline, cyanide bath [2]. Over a range of temperature and current density (or potential), deposits that were adherent, silver in colour and highly reflecting could be produced and their composition was in the range Cu 47–51%, Zn 8–12%, Sn 38–43%. Some of the consequences of operating outside the satisfactory ranges were also defined. In order to improve understanding of this complex plating bath, the study was extended with further experiments using solutions where the concentrations of Cu(I), Sn(IV) and Zn(II) as well as the concentrations of cyanide, hydroxide, carbonate and ‘Copper Glo’ additive were systematically varied.

It should be stressed that the concentrations of the bath components are never independent of time in a commercial plating line. The three metal ions are consumed in the alloy deposition process and since the ratio of the metals in the alloy is not the same as in solution, alloy plating leads to a change in both their absolute concentrations and the ratio of metal ions in solution. In addition, cyanide, hydroxide, carbonate [3] and Copper Glo are all active players in the overall chemistry of the bath. Free cyanide is formed during the cathodic reduction of the Cu(I) and Zn(II) species in

solution. It is also not completely stable to hydrolysis in the bath conditions and we have found experimentally that cyanide oxidation is the major anode reaction in the commercial electroplating bath. This oxidation is, however, a multielectron reaction and hence the cyanide balance taking into account cathode, anode and homogeneous reactions is difficult to assess. Likewise, hydroxide is formed in the reduction of the Sn(IV) complex in solution, but is also consumed in the anode reaction and is involved in homogeneous reactions, the hydrolysis of cyanide and the absorption of carbon dioxide from the atmosphere. Carbonate is likely to build up as it is a probable product of cyanide hydrolysis and oxidation and also results from CO<sub>2</sub> absorption. The chemistry of the Copper Glo has not been defined but in commercial practice, it is routinely added to the bath. Indeed, the organic component(s) of the Copper Glo are not fully disclosed although they are believed to be of the following structure:



The commercial additive may also be a mixture of such derivatives with different chain length alkyl or unsaturated groups.

## 2. Experimental details

The experimental equipment and procedures were described in the previous paper [1]. In all experiments described here, the electrodes were brass (68% Cu, 32% Zn) strips or silver coated brass strips and they were used only for one experiment before being discarded. The strips were 5 mm wide and cut from 100 mm × 75 mm brass plates supplied by Ossian Ltd. These plates were prepolished and supplied with a protective film. Before use, the film was removed and the plates were electrocleaned (1 A for 60 s) in an alkaline bath at 313 K and then acid etched. For experiments, the strips were mounted so that they dipped into the solution to a depth of 10 mm (to give a convenient electrode area of 1 cm<sup>2</sup>).

## 3. Results

### 3.1. Solutions containing only a single metal ion

Voltammograms were recorded for solutions of alkaline cyanide containing only one of the metal ions. In each case, the electrode is a fresh brass strip, area 1 cm<sup>2</sup> and the bath temperature was 333 K. The potential scan rate was 20 mV s<sup>-1</sup> and the scans were initiated from -1250 mV, just negative to the potential where corrosion of the brass occurs. For all three metal ion solutions, after recording a single potential scan to -2100 mV, some metal deposit was visible on the brass. However, only for the solution containing Sn(IV) does the voltammogram show a clear feature attributable to metal deposition. Figure 1 shows the voltammogram for Sn(IV). A reduction peak occurs at -1520 mV vs SCE and tin can be seen on the brass even at potentials positive to the peak (see later). Moreover, the peak current density of 5.5 mA cm<sup>-2</sup> is a significant value for the concentration of Sn(IV) in the solution although H<sub>2</sub> evolution is also visible at potentials around the peak and, hence, the contributions from the two simultaneous reductions cannot easily be deduced. The reverse scan also shows a cathodic peak, in fact larger than the

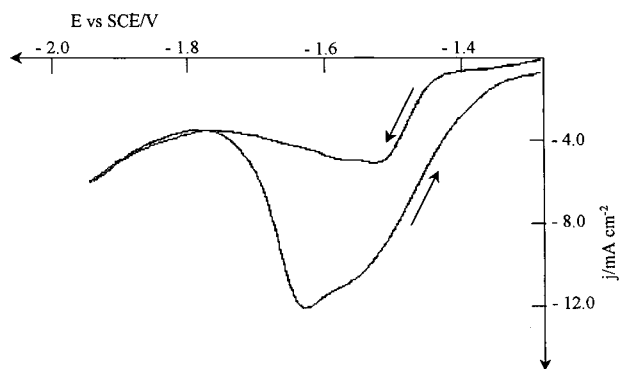


Fig. 1. Cyclic voltammogram for a solution of 24 mM Sn(IV) in 551 mM NaCN, 50 mM NaOH, 61 mM Na<sub>2</sub>CO<sub>3</sub> and 5 g l<sup>-1</sup> Copper Glo solution. Temperature 333 K. Potential scan rate 20 mV s<sup>-1</sup>.

forward sweep. This is a relatively unusual feature and probably reflects a reversible change to the tin surface, e.g. readsorption of an organic in the potential region from -1750 to -1650 mV. The voltammograms for the solutions of Cu(I) and Zn(II) show only a steady increase in current towards the negative limit and hydrogen evolution becomes increasingly vigorous through this part of the scan. The contribution from hydrogen evolution will depend on both potential and the metal being deposited since the kinetics of H<sub>2</sub> evolution on Cu, Sn and Zn as well as the brass substrate will be quite different. When cyclic voltammograms were recorded, anodic peaks for the reoxidation of deposited metal were not observed with any of the three metals.

The study was continued by a series of potentiostatic experiments with each of the three solutions. Table 1 summarizes the results for the Sn(IV) solution where the deposition time was limited to 30 s. It can be seen that at all potentials negative to -1500 mV, a substantial tin deposit was formed within this time. The best quality deposits were formed in the range from -1600 to -1800 mV but this is probably only a function of the deposit thickness. If the depositions were extended to 120 s, at all potentials the deposits became tarnished by a diffuse white film. The Table also reports the steady state currents at each potential and it can be seen that a plot of the steady state currents vs potential would show a peak at around -1650 mV. This is clearly the result of H<sub>2</sub> evolution (even in the steady state) which is visibly much diminished at more negative potentials before increasing again closer to the negative limit. A similar phenomenon was seen on sweep experiments once the brass substrate was covered by tin. Hydrogen evolution over a similar potential range was also noted for deposition of the Cu-Zn-Sn alloy from the commercial electroplating bath although only as a transient phenomenon [1]. It will be shown in the following section that H<sub>2</sub> evolution around -1600 mV is associated with the presence of both Sn(IV) and the Copper Glo additive in the plating solution and the potential range where it occurs is likely associated with adsorption of an organic on the deposit surface. Tables 2 and 3 report data from similar experiments with the Zn(II) and Cu(I) solutions. In general, it is clear that the rate of deposition of these

Table 1. Observations during potentiostatic experiments for the solution containing 24 mM Sn(IV) in 551 mM NaCN, 50 mM NaOH, 61 mM Na<sub>2</sub>CO<sub>3</sub> and 5 g l<sup>-1</sup> Copper Glo solution

E/mV vs SCE	$-j_{s,s}/\text{mA cm}^{-2}$	Deposit quality	H <sub>2</sub> evolution
-1400	1.9	poorly visible	some
-1500	5.3	reflecting but thin	significant
-1600	8.0	highly reflecting, uniform	vigorous
-1700	8.3	highly reflecting, uniform	vigorous
-1800	2.3	highly reflecting, uniform	minor
-1900	3.4	tarnished, uniform	some
-2000	6.7	tarnished, uniform	vigorous
-2100	15.0	tarnished, uniform	very vigorous

Brass strip electrode. Temperature 333 K. Deposition time 30 s

Table 2. Observations during potentiostatic experiments for the solution containing 46 mM Zn(II) in 551 mM NaCN, 50 mM NaOH, 61 mM Na<sub>2</sub>CO<sub>3</sub> and 5 g l<sup>-1</sup> Copper Glo solution

<i>E</i> /mV vs SCE	Deposition time/s	$-j_{s,s}$ /mA cm <sup>-2</sup>	Deposit quality	H <sub>2</sub> evolution
-1700	1000	2.2	very thin	little
-1800	600	3.0	thin but reflective	little
	1000		reflective, uniform	
-1900	540	1.6	thin but reflecting	little
-2000	480	2.0	highly reflecting, uniform	little
-2100	300	4.3	highly reflecting, uniform	some
-2200	120	7.0	highly reflecting, uniform	vigorous

Brass strip electrode. Temperature 333 K

Table 3. Observations during potentiostatic experiments for the solution containing 102 mM Cu(I) in 551 mM NaCN, 50 mM NaOH, 61 mM Na<sub>2</sub>CO<sub>3</sub> and 5 g l<sup>-1</sup> Copper Glo solution

<i>E</i> /mV vs SCE	Deposition time/s	$-j_{s,s}$ /mA cm <sup>-2</sup>	Deposit quality	H <sub>2</sub> evolution
-1700	420	1.5	uniform but thin	very little
-1800	360	6.0	uniform, highly reflecting	little
-1900	60	23.0	uniform, highly reflecting	very vigorous
-2000	60	41.3	uniform, highly reflecting	very vigorous
-2100	60		uniform, highly reflecting	very vigorous
-2200	60	75.5	uniform, highly reflecting	very vigorous

Brass strip electrode. Temperature 333 K

metals is much slower than tin; it is necessary to use a more negative potential and also usually a longer deposition time. In addition, it can be seen that the current densities are a very poor indication of the relative rates of metal deposition because of the hydrogen evolution. It is evident that H<sub>2</sub> evolution is much more vigorous on copper than on zinc and this results from a lower H<sub>2</sub> evolution overpotential.

Both the voltammetry and the potentiostatic experiments indicate that tin is easier to deposit than copper and zinc. Indeed, the voltammetry for tin deposition has a great similarity to that reported for the deposition of the Cu–Zn–Sn alloy [1]. In contrast, the Cu–Zn–Sn alloy with a metal ratio 48/10/42 deposits at potentials where the deposition of neither copper or zinc from solutions of single metals is possible. Moreover, the rate of alloy deposition appears comparable to that of tin. Therefore, it would appear that the deposition of tin is able to catalyse the deposition of Cu(I) and Zn(II) and allow the deposition of alloy.

### 3.2. Solutions containing Cu(I), Zn(II) and Sn(IV) with variable concentrations

Table 4 reports the composition (determined by EDS) of alloys electroplated on to silver coated brass strips from

solutions containing various molar ratios of Cu(I), Zn(II) and Sn(IV). In the first line of the table, the plating solution had the composition of the commercial alkaline cyanide bath. In subsequent entries, the concentration of one of the metal ions in solution has been varied while the concentration of all other bath constituents was held constant; the concentration of the chosen ion is either 0.5 or 1.5 times that in the standard solution. In all experiments, the temperature was 333 K, the current density was 6 mA cm<sup>-2</sup> and the electrodeposition was continued for ~150 s.

Several features of the results should be noted. Firstly, the atomic ratio of the metals in the alloy never reflects the concentration of metal ions in solution. For example, in the commercial bath, the molar ratio of Cu(I)/Zn(II)/Sn(IV) in solution is 59/27/14 while the ratio of metals in the alloy is Cu/Zn/Sn = 50/9/41. As noted in the previous paper, this is the clearest indication that the rates of the metal ion reductions are not mass transport controlled but determined by the rates of homogeneous chemical steps, probably ligand dissociation or exchange reactions. In general, the tin content in the alloy is always high and the zinc content low compared to their molar ratios in solution. This reinforces the conclusion above that tin is much easier to deposit than the other metals and has the role of facilitating the deposition of the other metals at least in the early stages of the alloy formation. Conversely the data suggest that zinc is a metal most difficult to deposit into the alloy. Secondly when the Cu(I) and Sn(IV) concentrations are varied, the trend in the metal content of the alloy is entirely predictable; an increase in relative amount of one ion leads to an increase in that metal in the alloy. It is, however, mainly the Cu and Sn contents which vary and zinc content of the alloy is quite constant. When the Zn(II) concentration is varied, it is the amounts of Zn and Sn which change. These trends are, at first sight, surprising since a consideration of the stability constants [4–6] for Cu(I), Zn(II) and Sn(IV) in hydroxide and cyanide media clearly leads to the conclusion that Cu(I) and Zn(II) are complexed by cyanide and Sn(IV) by hydroxide. But, again, it must be concluded that the

Table 4. Alloy compositions (determined by EDS) for layers deposited from solutions containing different metal ion concentrations. All solutions also contain 551 mM NaCN, 50 mM NaOH, 61 mM Na<sub>2</sub>CO<sub>3</sub> and 5 g l<sup>-1</sup> Copper Glo solution

Solution concentration/mM			Alloy composition/%		
Cu(I)	Zn(II)	Sn(IV)	Cu	Zn	Sn
102	46	24	50	9	41
153	46	24	62	7	31
51	46	24	32	10	58
102	69	24	53	15	32
102	23	24	52	4	44
102	46	36	45	8	47
102	46	12	62	9	29

Temperature 333 K. Silver undercoated brass strip electrodes. Current density 6 mA cm<sup>-2</sup>. Deposition time ~150 s

relative rates of reduction of the three metal ions are determined by kinetic factors and little by thermodynamics. It should be noted that the ratio of metal ion concentrations in solution is not the only parameter influencing the deposit composition. Current density also has a substantial influence [1] as do the concentrations of other bath constituents, see below.

During the depositions of the alloy (at  $6 \text{ mA cm}^{-2}$ ) the potential is always close to  $-2050 \text{ mV vs SCE}$ . Hydrogen evolution is observed during the deposition of alloy from all the solutions examined but its rate is clearly lower than would be observed from either copper or tin surfaces at the same potential (the currents for Cu and Sn cathodes at  $-2050 \text{ mV}$  would also be  $\gg 6 \text{ mA cm}^{-2}$ ). The low level of zinc in the alloy is having a substantial influence on the rate of  $\text{H}_2$  evolution.

All electroplates showed excellent adhesion. The visible appearance of the alloys plated, however, reflected their composition. The electroplated alloy layers with a composition close to that obtained from the commercial plating bath (i.e., Cu/Zn/Sn = 50/9/41) appeared uniform, were silver in colour and were highly reflecting. On the other hand, the deposits which were significantly richer in copper (Cu > 58%) were yellow, brown in colour and were less reflecting. In some conditions, it leads to "tiger stripe" electroplates; the metal deposit varies in thickness so as to give a striped feature with variable and alternating intensities of brown colouration. In addition, those deposits high in tin (Sn > 48%) had a hazy, tarnished appearance with a thin whitish film over the silver coloured metal. Surprisingly, the deposit which was high in zinc was the most highly reflecting.

The deposits were also examined by scanning electron microscopy. Figure 2(a)–(c) compares the micrographs for an electroplate with the composition obtained from the commercial bath with typical micrographs for deposits high in copper and tin (all containing Copper Glo). From the commercial bath composition, the deposit is almost featureless on the scale shown although the consequences of the linear scratches on the substrate remain visible. On the other hand, the deposits rich in copper and tin are clearly both made up of many small (dia.  $\approx 0.25 \mu\text{m}$ ), overlapping crystallites. The crystallites of tin rich deposits are angular while those of the copper rich deposits are hemispherical. This difference had been noted previously for samples taken from Hull cell experiments.

### 3.3. Influence of bath composition on the alloy composition

Table 5 reports the compositions of the alloys deposited from plating solutions where the concentrations of cyanide, hydroxide, carbonate and Copper Glo were varied in turn. In each experiment, the current density was  $6 \text{ mA cm}^{-2}$  and the deposition time was  $\sim 150 \text{ s}$ . It has previously been reported [1] that the commercial

plating bath leads to a Cu–Zn–Sn alloy with a metal ratio close to 48/10/42.

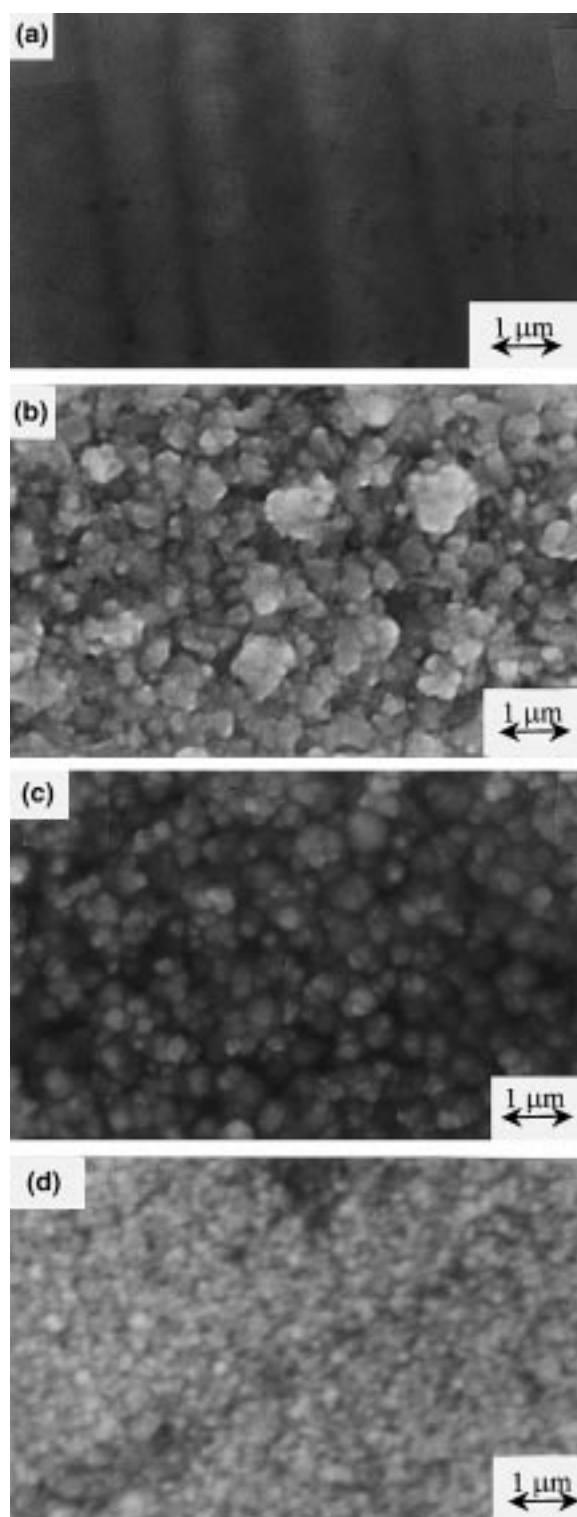


Fig. 2. Scanning electron microscopy for alloy deposits with the composition (a) Cu/Zn/Sn = 50/9/41 (b) Cu/Zn/Sn = 30/7/63 and (c) Cu/Zn/Sn = 64/15/21 (d) Cu/Zn/Sn = 50/9/41 but without Copper Glo. All plates were prepared on silver plated brass strip electrodes in the alkaline cyanide bath containing Cu(I), Zn(II) and Sn(IV) and 551 mM NaCN, 50 mM NaOH, and 61 mM  $\text{Na}_2\text{CO}_3$ . For (a)–(c), the bath contained  $5 \text{ g l}^{-1}$  Copper Glo solution. Temperature 333 K. Current density  $6 \text{ mA cm}^{-2}$ .

Table 5. Alloy compositions (determined by EDS) for layers deposited from solutions containing different concentrations of NaCN, NaOH, Na<sub>2</sub>CO<sub>3</sub> and Copper Glo solution. All solutions also contain 102 mM Cu(I), 46 mM Zn(II) and 24 mM Sn(IV)

Solution composition				Alloy composition/%		
CN <sup>-</sup> /mM	OH <sup>-</sup> /mM	CO <sub>3</sub> <sup>2-</sup> /mM	Copper Glo/g l <sup>-1</sup>	Cu	Zn	Sn
551	50	61	5	50	9	41
1058	50	61	5	27	5	68
419	50	61	5	67	9	24
551	129	61	5	53	19	28
551	16	61	5	30	6	64
551	50	188	5	51	8	41
551	50	61	20	52	9	39
551	50	61	10	52	8	40
551	50	61	1.25	51	10	39

Temperature 333 K. Silver undercoated brass strip electrodes. Current density 6 mA cm<sup>-2</sup>. Deposition time ~150 s

It can be seen that the free cyanide and free hydroxide concentrations have a substantial influence on the Cu/Sn ratio. The Cu/Sn ratio increases if the bath is either low in cyanide or high in hydroxide and decreases when the solution is high in cyanide or low in hydroxide. The zinc content is less sensitive to the CN<sup>-</sup>/OH<sup>-</sup> ratio although it is high in the concentrated hydroxide solution. The Cu/Sn ratios are readily understood in terms of speciation of the metal ions in the bath; Cu(I) is strongly complexed by cyanide while the Sn(IV) is complexed by the hydroxide [4–6]. All the deposits are strongly adherent and uniform but the appearance and morphology of these deposits appear to be totally determined by the alloy composition [3]. The copper rich deposits are reflecting but brown while the tin rich deposits are silver but slightly tarnished by a thin white film. By scanning electron microscopy, both types of deposit can be seen to be rough on a micrometre (μm) scale and have their characteristic morphology; both consist of many overlapping crystallites but the copper rich deposits have small hemispherical crystallites while the tin rich deposits are much more angular. In contrast, the deposit from the commercial bath is featureless in comparison.

On the one hand, neither the carbonate or organic additive concentrations seem to influence the alloy composition. On the other hand, the Copper Glo concentration has a very strong effect on the deposit appearance. Without the presence in the bath of the additive, the alloy deposit is rather poorly reflecting and it was found that the reflectivity increased with additive concentration. Indeed, the best deposits were plated from a bath containing 10 g l<sup>-1</sup> of Copper Glo solution (twice that in the commercial bath). This result was confirmed by scanning electron microscopy. Figure 2(d) shows a scanning electron micrograph of the deposit without Copper Glo solution. This may be compared with the SEM from the commercial bath, Figure 2(a). The fine grains are more apparent in the deposit from solution without additive.

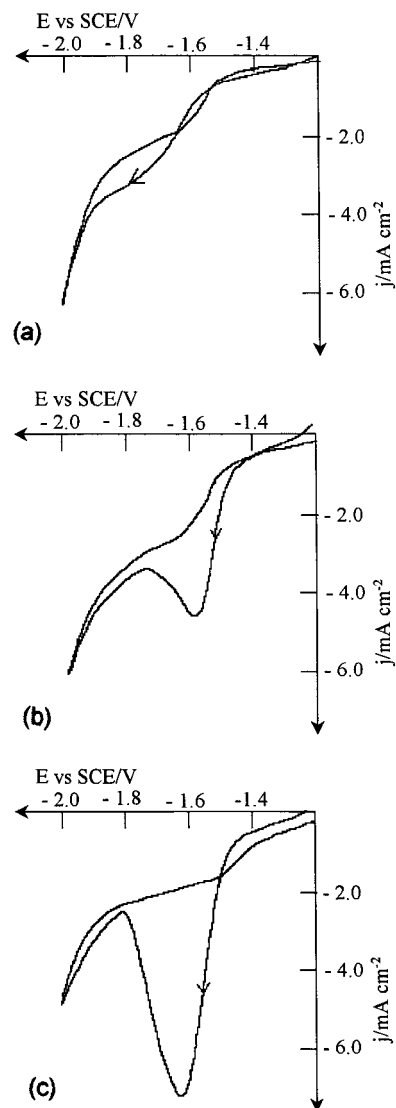


Fig. 3. Cyclic voltammograms for brass strip electrodes in the standard plating bath solution containing (a) 0 (b) 5 and (c) 10 g l<sup>-1</sup> of the Copper Glo solution. Potential scan rate 20 mV s<sup>-1</sup>. Temperature 333 K.

#### 3.4. Voltammetric studies of the role of the Copper Glo additive

Figure 3 shows cyclic voltammograms for unplated brass strip electrodes in plating bath solutions containing 0, 5 and 10 g l<sup>-1</sup> of the Copper Glo solution. It can clearly be seen that in the absence of additive, there is a reduction wave at -1600 mV and this reduction process obviously leads to an alloy layer on the electrode surface. With the sequential addition of aliquots of Copper Glo, the response appears to consist of a peak superimposed onto this reduction wave and the peak becomes larger upon further additions of Copper Glo, see Figure 4. With 5 and 10 g l<sup>-1</sup> of the Copper Glo solution this peak is rather symmetrical as might be expected for a process related to adsorption/desorption. In fact, much of the charge associated with this peak is associated with H<sub>2</sub> evolution as a pulse of the gas is seen

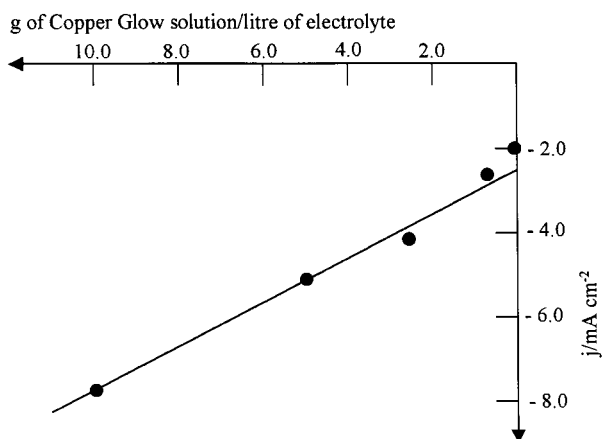


Fig. 4. Plot of peak current density against amount of Copper Glo solution added to the bath.

leaving the electrode as the potential is scanned through the range of the peak. It may also be noted that the reverse scans on the voltammograms show little variation with the amount of additive present.

The voltammetry of Copper Glo at brass and alloy plated brass electrodes in alkaline cyanide medium but in the absence of the metal ions, Cu(I), Zn(II) and Sn(IV), was also investigated. Voltammograms for such solutions do not show reduction peaks or waves prior to the negative potential limit. Hence, the reduction peak does not correspond to the direct cathodic reduction of Copper Glo and the conditions for  $H_2$  evolution around  $-1600\ mV$  are not reproduced. Moreover, when experiments were carried out on solutions containing single metal ions, only in the case when Sn(IV) was present was a similar peaked response observed. Indeed, it was found throughout the investigation that the cathodic peak was most pronounced for alloy deposits which contained a high tin content (e.g., those from baths high in cyanide or low in hydroxide ion) although the cathodic peak was also a characteristic in voltammograms for the commercial alloy electroplating bath. This may be illustrated by a series of experiments where the cyanide concentration was increased from 418 mM to 1060 mM. The tin content of the alloy was found to increase steadily while during cyclic voltammograms the peak current density for the process at  $-1600\ mV$  also increased.

It was also considered interesting to see whether other amine oxides reproduced the voltammetric characteristics of Copper Glo. Two such compounds were investigated, trimethylamine N-oxide and dimethyloctylamine N-oxide. When voltammograms were recorded for the N-oxides in sulfate medium pH 12, again no reduction was observed at either Pt or C cathodes. In addition, when these N-oxides (in concentrations up to  $5\ g\ l^{-1}$ ) were employed instead of Copper Glo as additives in the alkaline cyanide plating bath, neither compound led to the observation of a cathodic peak around  $-1600\ mV$ . Furthermore, neither compound led to transient hydrogen evolution close to

$-1600\ mV$  nor improved the reflectivity of the alloy deposits. It must be concluded that the N-oxide group is not the active functional group in the additive molecule. Its role is probably only to enhance the solubility of the additive in aqueous solutions; N-oxides are commonly very soluble in aqueous solutions.

### 3.5. Voltammetric studies in media with variable carbonate, cyanide and carbonate

Figure 5 reports linear potential scan experiments for the commercial alloy plating bath with three different hydroxide ion concentrations. The concentrations of the other components are constant and all solutions contain  $5\ g\ l^{-1}$  Copper Glo solution. The solutions containing 50 mM and 130 mM hydroxide ion give similar voltammograms which have the form consistent with a peak at  $-1650\ mV$  superimposed on a reduction wave, see above. Certainly, significant reduction of metal ions to the alloy does not commence until potentials negative to  $-1550\ mV$  vs SCE. In the solution with a low hydroxide ion concentration, cathodic current is observed at potentials negative to  $-1400\ mV$  and the response appears to consist of a reduction wave with  $E_{1/2} = -1440\ mV$  and a peak at about  $-1650\ mV$ . Again, the reduction current at potentials just negative to  $-1400\ mV$  leads to visible alloy deposition and it must be concluded that metal is deposited more readily from the bath with low hydroxide concentration. This might be expected for the reduction of Sn(IV) since this ion is complexed by hydroxide. Since an alloy, albeit one with a high tin content is deposited from this bath, it again appears that the reduction of Sn(IV) to Sn is important in the early stages of alloy layer formation.

A similar set of voltammograms was recorded for solutions with variable cyanide concentrations. The solution with low cyanide (418 mM) which gave a deposit low in tin content gave a voltammogram with a reduction wave but without the cathodic peak. Also, the voltammogram for the high cyanide (1060 mM) solution which gave a deposit high in tin, showed metal deposition at potentials positive to  $-1500\ mV$ . These data reinforce earlier observations that tin and tin rich alloys can be deposited at less negative potentials than the commercial alloy. Also, the observation of transient hydrogen evolution and a peak at  $-1650\ mV$  during voltammetry also correlate with a high tin content. Indeed, on tin itself, hydrogen evolution and a peak in the current around  $-1600\ mV$  are observed in the steady state, see Table 1.

Variation of the carbonate concentration in the bath did not lead to a change in the voltammetric response.

## 4. Discussion

The results in Tables 4 and 5 are consistent with the conclusion that the composition of the alloy deposited is determined almost entirely by the availabilities of the

Cu(I), Zn(II) and Sn(IV) in a form suitable for reduction at the substrate in the plating bath. This can be controlled either through the concentrations of the

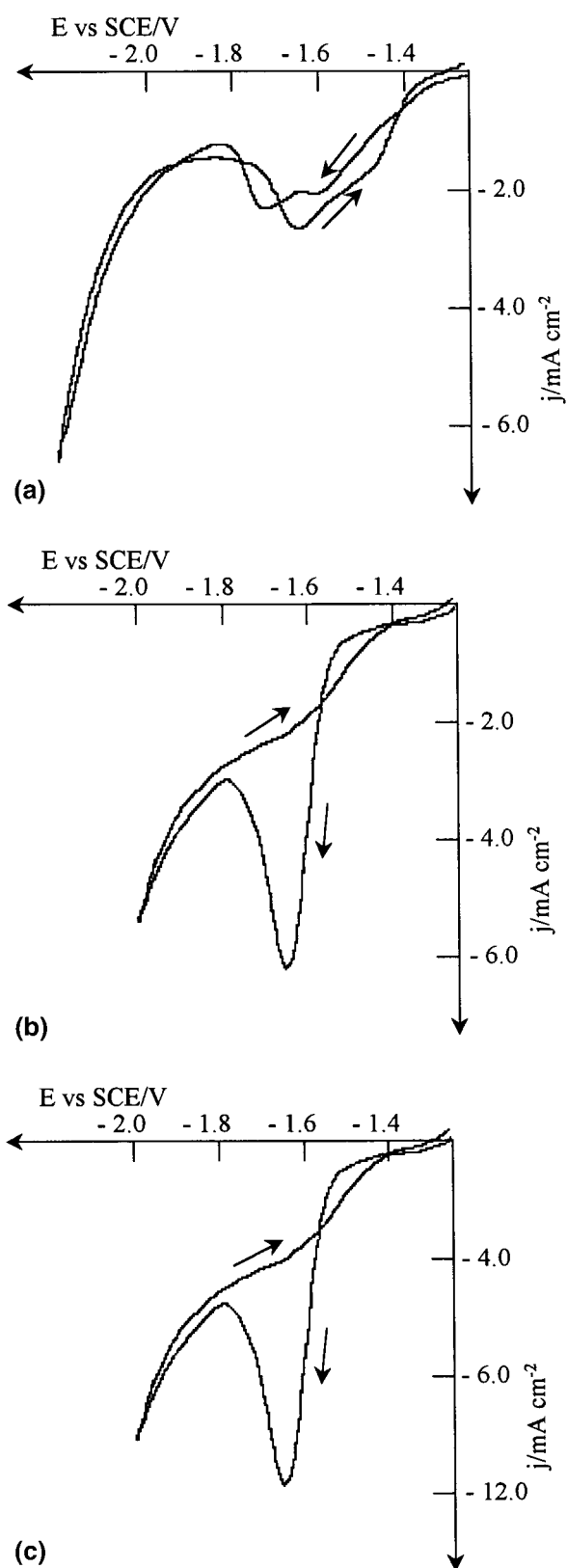


Fig. 5. Linear potential scan experiments for brass strip electrodes in the alkaline cyanide bath for Cu–Zn–Sn alloy containing (a) 16 mM (b) 50 mM and (c) 130 mM hydroxide ion. Potential scan rate  $20 \text{ mV s}^{-1}$ . Temperature 333 K.

metals themselves or the ligands which complex them, particularly the cyanide which controls the Cu(I) and hydroxide which controls the Sn(IV). The commercial plating bath composition leads to an alloy with the composition Cu 47–51%, Zn 8–12% and Sn 38–43%. Changes in the concentrations of either the metal ions or the complexing agents can lead to alloys with Cu or Sn contents  $> 60\%$  and there are consequent changes in the appearance of the deposits and morphologies on a  $1 \mu\text{m}$  scale when examined by scanning electron microscopy. The quality of the deposits is generally good; uniform and adherent deposits are obtained over a surprisingly wide range of conditions in this alkaline cyanide bath. However, the desired silver colour requires control of the alloy composition and an acceptable rate of deposition necessitates the use of a temperature above ambient, usually 333 K. The Copper Glo additive has the role of improving reflectivity without changing the composition of the alloy. It should again be noted that neither temperature or additive concentration appear to influence the deposit composition.

Hydrogen evolution has an important role in the behaviour and performance of the bath. The rate of  $\text{H}_2$  evolution during steady state alloy plating (i.e., deposit thickening) certainly determines the current efficiency for the deposition of the alloy. We will put forward below the hypothesis that it is also implicated in the mechanism by which the additive enhances the reflectivity of the deposit. It should be recognised that  $\text{H}_2$  evolution is a possible reaction over all the potential range investigated and all the potential range where alloy can be deposited. The equilibrium potential for  $\text{H}_2$  evolution in the alkaline medium is  $\sim -1100 \text{ mV vs SCE}$  and negative to this potential, the amount of hydrogen evolved is determined by kinetics. The kinetics of  $\text{H}_2$  evolution will depend on the metal surface exposed to the bath and will be quite different on the substrate and the alloy and would be expected to vary with the composition of the alloy. Certainly, the rate of  $\text{H}_2$  evolution increases along the series  $\text{Zn} < \text{Cu} < \text{Sn}$  and this trend appears to be followed in alloy composition during deposit thickening.

In the deposition of the alloy, the reduction of Cu(I), Zn(II) and Sn(IV) are also occurring at potentials significantly negative to those predicted by thermodynamics and hence the electron transfer processes are all being driven by significant overpotentials. In the conditions employed for commercial plating, however, the rate of deposition is slightly effected by mass transfer conditions and the main control is by the rate of homogeneous reactions in solution, probably changes to the speciation of the metals. This is the reason that an elevated temperature is essential to obtaining an acceptable rate of deposition.

The tin appears to have a key role in the mechanism of deposition of the alloy. Certainly, it was the only metal easily deposited from solutions containing only a single metal and the voltammetry also provides compelling evidence that the reduction of Sn(IV) facilitates

the reduction of Cu(I) and Zn(II) and hence the formation of the alloy. The presence of tin, in addition to Copper Glo, is also essential to produce voltammograms with the cathodic peak at  $-1600$  mV which correlates well with the improvement in reflectivity of the alloy. It has been noted that this peak is associated with  $H_2$  evolution as a transient phenomenon; it is observed only over a narrow potential range and stops after a short period of alloy deposition if the potential is held in this potential region. Almost certainly, this behaviour is associated with adsorption of an organic molecule(s) over this potential range and it could be that this adsorption is more favourable on a tin containing surface since the additive only leads to characteristic behaviour for such surfaces. During many experiments, e.g. constant current or constant potential deposition, this  $H_2$  evolution occurs only for a short period during the early stages of deposition. This suggests that the additive acts by influencing the very early stages of metal deposition, perhaps through the rate of formation of nuclei of the alloy phase.  $H_2$  evolution is occurring, it will influence the current distribution over the surface of the substrate and make it more uniform. In addition, certainly during constant current plating, the rate of reduction of the metal ions will be reduced by the occurrence of the  $H_2$  evolution. Thus a possible mode of action for the additive is to slow down nucleation and early growth of the alloy phase (the  $H_2$  evolution will

contribute to the current) and hence to create a basis for further growth of a deposit smooth on a submicrometric scale. Alternatively, the very first step in alloy formation could be the deposition of tin rich centres which then facilitate the reduction of Cu(I) and Zn(II) species to form the alloy and while the alloy depositing is rich in tin, it catalyses  $H_2$  evolution.

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