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THE ELECTRODEPOSITION OF METALS FROM THEIR TRIFLUOROACETATE–AMIDE BATHS

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Abstract – This paper will deal with the electrodeposition of copper and nickel from the $Cu(CF_3COO)_2$–$HCONH_2$ bath, $Ni(CF_3COO)_2$–$HCONH_2$ bath, $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ bath. The properties of these baths and the mechanism of the electrodeposition of copper and nickel from these baths were studied. While solvolysis occurs in the $HCONH_2$ bath, it does not occur in the $HCON(CH_3)_2$ bath. A complex is formed in each bath. Since the bond between the metallic ion and the solvent in the $HCON(CH_3)_2$ bath is stronger than that in the $HCONH_2$ bath, and since the dielectric constant of the solvent in the former is also lower than in the latter, is difficult to electrodeposit metal and Cu_2O is formed at cathode in the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath. The specific conductance in the $HCON(CH_3)_2$ bath is lower than that in the $HCONH_2$ bath. It is possible to obtain a better copper electrodeposit over a wider range of current density in the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath containing citric acid than in the same bath containing no citric acid. This range almost coincides with that in the $Cu(CF_3COO)_2$–$HCONH_2$ bath. While it is possible to obtain better nickel electrodeposit in $Ni(CF_3COO)_2$–$HCONH_2$ and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths containing appropriate additives, the range of current density which permits one to obtain a superior electrodeposit in the latter bath is narrow. The electrodeposit of nickel or copper obtained from the $HCONH_2$ and $HCON(CH_3)_2$ baths has a granular structure. The values of η_c, E_c, and b_c in the copper electrodeposition reaction from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–200 g/l citric acid bath are higher than those in the same reaction from the $Cu(CF_3COO)_2$–$HCONH_2$ bath, while the values of i_{oc} and α_c are lower, so the electrodeposition of copper from the former can be said to be more difficult. On the other hand, the value of n is always about 1 for both the baths. It may be concluded in view of this fact that the deposition of copper from $HCONH_2$ and $HCON(CH_3)_2$ baths takes place through Cu^+ and that the deposition of nickel from $HCONH_2$ bath takes place through Ni^+.

INTRODUCTION

The present author has been studying the electrodeposition of metals from non-aqueous solutions of metal trifluoroacetates[1, 2].

$HCONH_2$ has a high boiling point and a high dielectric constant and readily forms complex ions with metal ions. $HCON(CH_3)_2$ is a polar aprotic solvent; it has a comparatively low melting point and a comparatively high boiling point amoung the amide solvents. It can be expected that this solvent would also be useful for the electrodeposition of very base metals, because the solvent, lacking in active hydrogen, does not evolve H_2 simultaneously with the metallic electrodeposition from this solution.

In the present experiment, the author investigated the properties of $Cu(CF_3COO)_2$–$HCONH_2$, $Ni(CF_3COO)_2$–$HCONH_2$, $Cu(CF_3COO)_2$–$HCON(CH_3)_2$, and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths, the electrodeposition of copper and nickel from these baths, and the mechanism of the electrodeposition of copper and nickel from these baths.

EXPERIMENTAL

Reagent

Formamide. For the measurement of the conductance, guaranteed reagent-grade formamide containing about 0.02% moisture was used. For the electrodeposition and the measurement of the overvoltage, commercial first-grade reagent formamide containing about 0.12% moisture was used.

$HCON(CH_3)_2$. A reagent grade containing about 0.003% moisture was used.

$Cu(CF_3COO)_2$ *and* $Ni(CF_3COO)_2$. These substances were prepared by the neutralization method from copper hydroxide and nickel hydroxide with trifluoroacetic acid. The purities of the corresponding products were 99.4% and 99.8% respectively.

Measurement of the conductance

The electrolytic conductance of $Cu(CF_3COO)_2$–$HCONH_2$, $Cu(CF_3COO)_2$–$HCON(CH_3)_2$, $Ni(CF_3COO)_2$ $HCONH_2$, and $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ solutions was determined by the use of a Yanagimoto electrolytic conductometer My-7. Before the measurement the solutions to be measured were kept for about 1 h at 50°C.

Electrodeposition

In the case of copper electrodeposition, two copper plates and one iron plate were used as anode and cathode respectively. For nickel deposition, two nickel plates and one copper plate were used as anode and cathode respectively. These electrodes were pretreated by the following method: 1. Pickled in alkaline solution in a day, 2. Washed with distilled water, 3. Etched in acid solution [Ni: nitric acid (30 ml)–sulfuric acid (10 ml)–phosphoric acid (10 ml)–acetic acid (50 ml) solution at 90°C, Cu: nitric acid (100 g/l) sulfuric acid (80 g/l)–hydrochloric acid

(25 g/l) aqueous solution at room temperature, Fe: Oxalic acid (25 g/l)–hydrogen peroxide (13 g/l) sulfuric acid (0.1 g/l) aqueous solution at room temperature], 4. Washed with distilled water and then ethanol, 5. Weighed. Nitrogen was passed through formamide or $HCON(CH_3)_2$ for about 30 min. A definite amount of the $Cu(CF_3COO)_2$ or $Ni(CF_3COO)_2$ was dissolved in the formamide or $HCON(CH_3)_2$ solution to give a bath used for the electrodeposition. The bath was stirred at a definite rate with magnetic stirrer.

The thickness of the electrodeposited layer was about 5 μ, the thickness being calculated from the amount electricity used for the deposition. A current efficiency is measured by gain of weight.

Observation of the electrodeposited surface and the electrodeposited layer

For these observations, a metallurgical microscope was used.

Measurement of the overvoltage

The overvoltage of copper or nickel electrodeposition was measured at 30–70°C for the $Cu(CF_3COO)_2$–$HCONH_2$, $Ni(CF_3COO)_2$–$HCONH_2$, and Cu- $CF_3COO)_2$ citric acid (200 g/l)–$HCON(CH_3)_2$ baths containing 50–400 g $Cu(CF_3COO)_2$ or $Ni(CF_3COO)_2$ per liter respectively. The overvoltage of hydrogen evolution was measured at 50°C in H_2O, $HCONH_2$, and $HCON(CH_3)_2$ baths containing CF_3COOH (0.1 N). Measurement was made by the current-interrupter method, with stirring at a definite rate. A platinized–platinum electrode (length, 3 mm; dia, 0.3 mm) was used as a reference electrode for the measurement of the overvoltage. A current-interrupter, Type CI-2515, made by the Hokuto Electric Works Co., Ltd., was used.

RESULTS AND DISCUSSION

Solvolysis

In the $Ni(CF_3COO)_2$–$HCONH_2$ solution, a light yellow-green precipitate is formed by the reaction of $Ni(CF_3COO)_2$ with $HCONH_2$. The reaction becomes more remarkable with a rise in the bath temperature and with an increase in the $Ni(CF_3COO)_2$ concentration.

When the reaction product was filtered, an almost colorless filtrate was obtained. It was found by the gas-chromatographic analysis of this solution and the gravimetrically analysis of the precipitate that the reaction shown in (1) takes place in the $Ni(CF_3COO)_2$–$HCONH_2$ solution.

$$M(CF_3COO)_2 + 4HCONH_2 \rightarrow M(HCONH)_2 \times 2HCONH_2 + 2CF_3COOH \quad (1)$$

where M represents Cu or Ni.

As same as in the $Ni(CF_3COO)_2$–$HCONH_2$ solution, a blue white precipitate produced after the heating at about 90°C, in the $Cu(CF_3COO)_2$–$HCONH_2$ solution and CF_3COOH was also detected in the filtrate when the precipitates were filtered. Therefore, it is likely that the reaction shown by (1) also takes place in this solution.

In a $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ saturated solution at 20°C, crystals were precipitated after several days. And, after the heating at about 90°C, of $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ solution, a precipitate produced in the solution. It was found by the gravimetrically analysis and the measurement of *ir* spectra that these precipitates were $Ni(CF_3COO)_2 \cdot 4HCON(CH_3)_2$ and $Cu(CF_3COO)_2 \cdot 4HCON(CH_3)_2$ respectively.

Therefore, the measurement of the specific conductance of these solutions and the electrodeposition of metals from the solutions were studied on the conditions (suitable bath temperature and concentration of metal trifluoroacetates) that the precipitate-reaction did not occur in the solutions.

Specific conductance

Figure 1 shows the specific conductance of the $Cu(CF_3COO)_2$–$HCONH_2$ and $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ solution at 50°C.

The specific conductance of the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ solution was almost the same as that of the $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ solution and, the specific conductance of the $Cu(CF_3COO)_2$–$HCONH_2$ solution was almost the same as that of the $Ni(CF_3COO)_2$–$HCONH_2$ solution. The specific conductances of the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ solution and the $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ solution are both about one quarter of those of the $Cu(CF_3COO)_2$–$HCONH_2$ solution and the $Ni(CF_3COO)_2$–$HCONH_2$ solution.

It seems that more viscous $HCONH_2$ solution has a higher electrolitic conductance than the less viscous $HCON(CH_3)_2$ solution, mainly because the dielectric constant of $HCONH_2$, 110, is about three times that of $HCON(CH_3)_2$, 37.

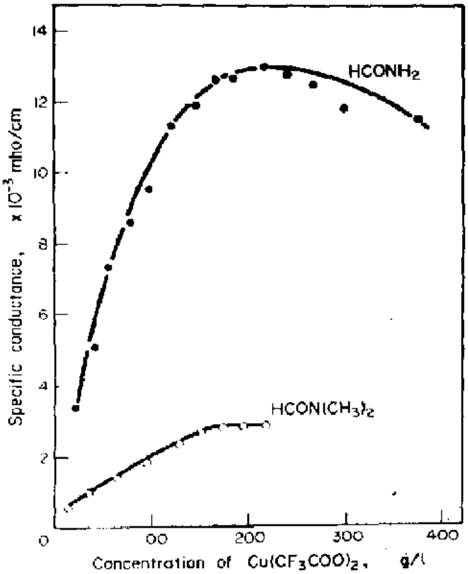

Fig. 1. Specific conductance of $Cu(CF_3COO)_2$–$HCONH_2$ solution and $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ solution at 50°C.

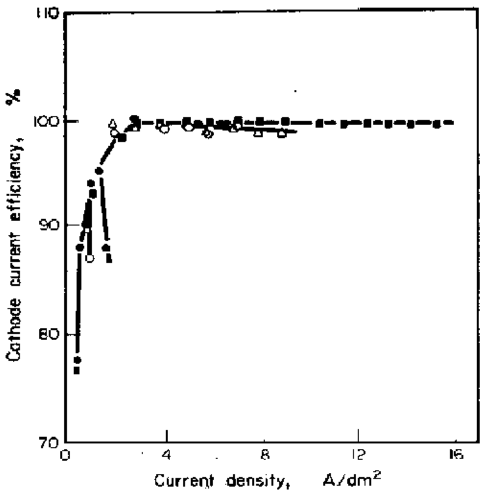

Fig. 2(1). Cathode current efficiency as a function of current density for copper deposition from $Cu(CF_3COO)_2$–$HCONH_2$ bath at 40°C. $Cu(CF_3COO)_2$(g/l): ● : 20, ○ : 100, △ : 200, ■ : 400.

Electrodeposition

(1) *Copper electrodeposition.* In the $HCON(CH_3)_2$ bath, the anode current efficiency was always about 100 per cent, irrespective of the $Cu(CF_3COO)_2$ concentration and the bath temperature.

In the $HCONH_2$ bath, the anode current efficiency was found to be more than 100 per cent irrespective of the $Cu(CF_3COO)_2$ concentration and the bath temperature. The efficiency even exceeded 110 per cent at a low current density. This efficiency is attributable to the chemical reaction of copper with the CF_3COOH formed by the reaction given by (1).

Figure 2 shows an example of the current density–cathode current efficiency curve of copper deposition from the $Cu(CF_3COO)_2$–$HCONH_2$ bath. In the $HCONH_2$ bath, the cathode current efficiency was close to 100 per cent irrespective of the $Cu(CF_3COO)_2$ concentration.

In the other hand, in the $HCON(CH_3)_2$ bath, the cathode current efficiency was also scarcely affected by the bath temperature, and decreased down to about 10 per cent at low current density with an increase in the $Cu(CF_3COO)_2$ concentration.

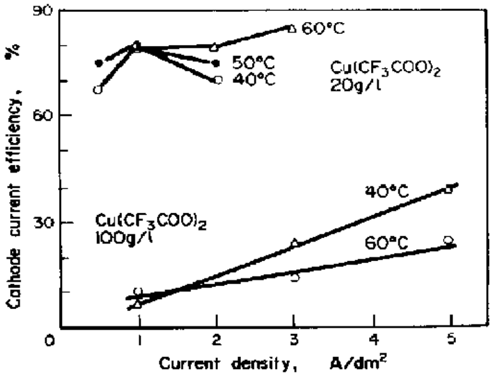

Fig. 2(2). Cathode current efficiency as a function of current density for copper deposition from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath.

No gases evolved from the anode and cathode, but during electrolysis a yellowish-brown precipitate was produced at the cathode. Elementary analysis of this precipitate showed C:6.89%, H:0.88%, and Cu:55.0%; X-ray diffraction showed that it was mainly composed of Cu_2O. It may be that the low cathode current efficiency is caused by low adhesion of the Cu_2O.

Moreover, gas chromatographic analysis of the cathode solution proved the existence of $(CF_3CO)_2O$.

Therefore, the following reaction (2) can be said to have occured at the cathode, resulting in a decrease in the cathode current efficiency:

$$2Cu(CF_3COO)_2 + 2e \rightarrow Cu_2O + (CF_3CO)_2O + 2CF_3COO^- \quad (2)$$

In view of this fact, it seems that it is difficult for copper electrodeposition to occur from a $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath because the copper ion forms a stable complex with $HCON(CH_3)_2$ if the $Cu(CF_3COO)_2$ concentration is high.

We have assumed that, if this stable copper complex were broken, it would be possible to facilitate the copper electrodeposition from the bath; we thus tentatively added citric acid, a complex agent, to the bath.

The increased addition of citric acid increases the cathode current efficiency as in Fig. 3. It is apparent that the addition of citric acid is effective for efficient copper electrodeposition in the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$ bath and that the best amount of citric acid to be added (200 g/l) is in a ratio

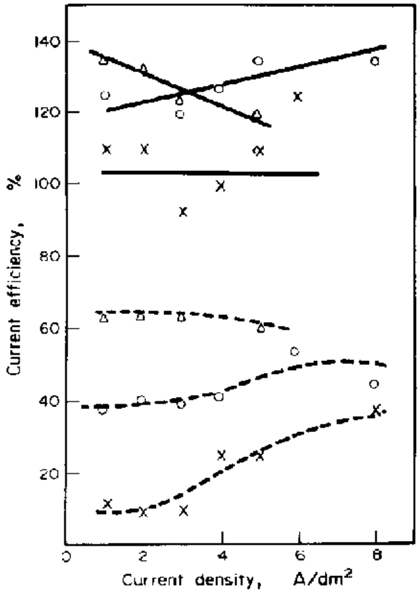

Fig. 3. Cathode and anode current efficiencies as a function of current density for copper deposition from the $Cu(CF_3COO)_2$–(100 g/l)–$HCON(CH_3)_2$ bath containing citric acid at 50°C. Anode: ———, Cathode: – – – –, citric acid (g/l): × : 20, ○ : 100, △ : 200.

Table 1. The range of current density for the bright and smooth copper deposit from the $Cu(CF_3COO)_2$–citric acid (200 g/l)–$HCON(CH_3)_2$ bath (unit of current density : A/dm^2)

Bath temp. (°C)	$Cu(CF_3COO)_2$ (g/l)			
	20	100	300	500
40	0.5–1.0	1.0–2.0	1.0–4.0	2.0–7.0
50	1.0	1.0–3.0	2.0–5.0	3.0–7.0
60	1.0	2.0–5.0	3.0–7.0	2.0–11

Table 2. The range of current density for the bright and smooth copper deposit from the $Cu(CF_3COO)_2$–$HCONH_2$ bath (unit of current density : A/dm^2)

Bath temp. (°C)	$Cu(CF_3COO)_2$ (g/l)			
	20	100	200	400
30	0.2–1.0	1.0–4.0	1.0–6.0	1.0–8.0
40	0.6–1.0	2.0–4.0	2.0–8.0	2.0–11.0
50	0.5–1.0	3.0–5.0	3.0–8.0	4.0–12.0

of 1 mol $Cu(CF_3COO)_2$ to more than 2 mol citric acid. In the solution with citric acid (200 g/l), while the anode current efficiency was higher than 100 per cent irrespective of the $Cu(CF_3COO)_2$ concentration and the bath temperature, the cathode current efficiency was affected by the $Cu(CF_3COO)_2$ concentration; it amounted to 75 per cent in 100–500 g/l $Cu(CF_3COO)_2$ baths and to 85 per cent in the bath with a $Cu(CF_3COO)_2$ concentration lower than 100 g/l at 60°C for a high current density. It seems that the anode current efficiency exceeds 100 per cent, because the anode is also chemically dissolved in the bath's acid (citral acid). The evolution of hydrogen gas from the cathode lowered its current efficiency.

Tables 1 and 2 show the range of current density within which a bright and smooth copper deposit can be obtained from a $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid (200 g/l) bath and $Cu(CF_3COO)_2$–$HCONH_2$ bath respectifely.

These ranges in the case of the $HCON(CH_3)_2$ bath containing citric acid are remarkably wider than those in the case of the bath without citric acid are almost equal to those in the case of the $HCONH_2$ bath with the same $Cu(CF_3COO)_2$ concentration.

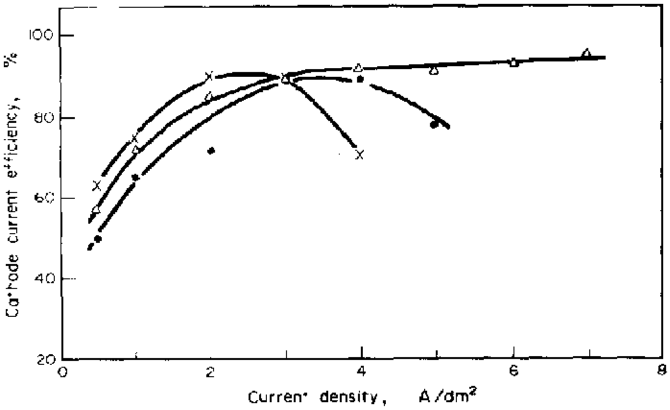

Fig. 4(1). Cathode current efficiency as a function of current density for the $Ni(CF_3COO)_2$ (100 g/l)–$HCONH_2$ bath. Bath temp. (°C): × : 50, △: 60, ●: 70.

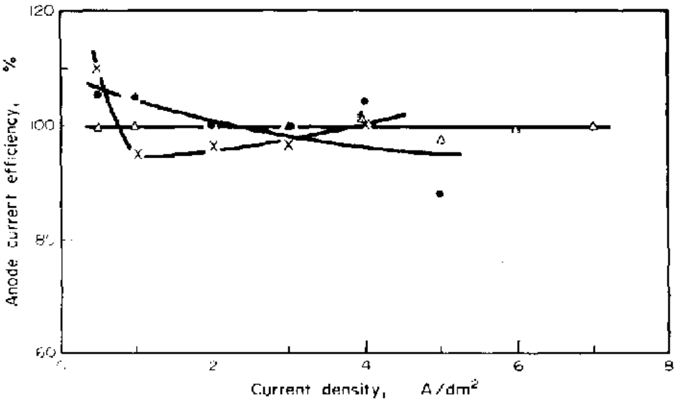

Fig. 4(2). Anode current efficiency as a function of current density for the $Ni(CF_3COO)_2$ (100 g/l)–$HCONH_2$ bath. Bath temp. (°C): × : 50, △: 60, ●: 70.

Table 3. The range of current density for the bright and adherent nickel deposit from the $Ni(CF_3COO)_2$–$HCONH_2$ bath (unit of current density : A/dm^2)

Bath temp. (°C)	$Ni(CF_3COO)_2$ (g/l)			
	80	100	150	200
40	1.0–2.0		0.5–1.0	
50	1.0–2.0	1.0–2.0	0.5–2.0	1.0–2.0
60		0.5–2.0		
70		0.5–4.0		

(2) *Nickel electrodeposition*. An example of the current density–current efficiency curve for the nickel deposition from the $Ni(CF_3COO)_2$–$HCONH_2$ bath is shown in Fig. 4. With the increase in the $Ni(CF_3COO)_2$ concentration, the cathode current efficiency increased, but the anode current efficiency tended to decrease. When the $Ni(CF_3COO)_2$ concentration was 80–100 g/l, the anode current efficiency was close to 100 per cent irrespective of the bath temperature. However, the cathode current efficiency was low at 50°C and 70°C when the current density was high. Only at 60°C was the efficiency about 90 per cent at high current density. The discharge of the H^+ formed by the dissociation of CF_3COOH in the bath occured on the cathode during the electrolysis in the $Ni(CF_3COO)_2$–$HCONH_2$ bath, as in the case of the $Cu(CF_3COO)_2$–$HCONH_2$ bath, resulting in the evolution of a small amount of hydrogen. From the $Ni(CF_3COO)_2$–$HCONH_2$ bath, the evolution of carbon dioxide gas occurred from the anode. However, the amount of carbon dioxide evolved was much smaller than that of the gas evolved from the cathode.

The deposits from the $Ni(CF_3COO)_2$ $HCONH_2$ bath were easily peeled off from the substrate when the $Ni(CF_3COO)_2$ concentration or the bath temperature was low. Table 3 shows the current density region in which a lustrous and adherent nickel deposit is obtained.

Table 4 shows some results obtained on nickel deposition from $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ baths with additives. The additives chosen were such that could dissolve the anode (Ni plate) and/or form a metal complex ion with the metal ion in the bath.

From Table 4 it is apparent that the nickel electrodeposition from a $Ni(CF_3COO)_2$–$HCON(CH_3)_2$ bath is promoted by adding NH_4Cl, sulfamic acid, H_3BO_3, or CCl_3COOH to the bath. It seems that as chloride is dissolved in $HCON(CH_3)_2$ with more difficulty than in $HCONH_2$, both nickel deposition and anode dissolution are more difficult in a $HCON(CH_3)_2$ bath than in a $HCONH_2$ bath.

Observation of the electrodeposited surface and the electrodeposited layer

The electrodeposited surfaces of the deposits of copper and nickel obtained from the $HCONH_2$ bath and the $HCON(CH_3)_2$ bath are very smooth and consist of very fine grains. A cracked deposited surface is obtained from the $HCON(CH_3)_2$ bath containing $AlCl_3$ or CCl_3COOH.

The electrodeposited layers of the deposits of copper and nickel have a granular structure irrespective of the bath temperature, the current density, and the metal trifluoroacetate concentration. An example of the electrodeposited surface and the electrodeposited layer was shown in Fig. 5.

Mechanism of the electrodeposition

From the decay curve of the overvoltage 4 ms after the interruption of the electrolytic current, the resistance polarization was subtracted. The remainder was assumed to be the activation overvoltage (η_c).

The electrodeposition of metals from the solvated metal complex ions is generally complicated. This experiment was based upon the thought that the charge-transfer reaction is rate-determining within the range of current density (*ie* The Tafel region) with a straight-line relation between the current density and the activation overvoltage.

The apparent exchange current density (i_{oc}) of copper and nickel deposition was obtained by extrapolating the η_c in the relation of η_c–i_c (current density) to 0.

On the Tafel curves, (3) and (4) hold among the apparent valence (n), the apparent transfer coefficient (α_c), i_{oc}, the apparent standard rate constant (K_{SR}) of copper and nickel depositions and the concentration of Cu^{2+} or Ni^{2+}, C_o mol/l:

$$i_c = i_{oc} \exp(-\alpha_c F n \eta_c / RT) \tag{3}$$

$$i_{oc} = nFK_{SR}C_o(1 - \alpha_c) \tag{4}$$

If the plot of $\log i_{oc} - \log C_o$ becomes linear, its slope is equal to $(1 - \alpha_c)$ as is given by (4). On the other hand, the slope of the Tafel line (b_c) are equal to $2.393 \times RT/\alpha_c nF$ as is given by (3). Therefore, $\alpha_c n$ was de-

Table 4. Electrodeposition of nickel from $Ni(CF_3COO)_2$ (20 g/l)–$HCON(CH_3)_2$ bath with additives at 40°C

Additive (g/l)	Current density (A/dm^2)	Current efficiency (%)		Deposit
		cathode	anode	
No addition	0.5–1.0	56–95	12–65	black
NH_4Cl 4.0	0.5–2.0	28–78	100–110	bright
H_3BO_3 4.0–22	1.0	92–42	31–62	bright
Sulfamic acid 4.0–16	1.0	17–9.7	16 12	bright
Citric acid 4.0	0.5–1.0	10–16	5.6–3.1	grey
LiCl 4.0	0.5–1.0	60–6.3	104–103	black
$AlCl_3$ 4.0	0.5–2.0	59–91	105–107	bright
CCl_3COOH 2.0 6.0	0.5–2.0	65–63	6.7–12	bright

Fig. 5(1). Surface of nickel deposit obtained from the Ni(CF$_3$COO)$_2$ (100 g/l)–HCONH$_2$ bath at 1.0 A/dm^2 at 60°C.

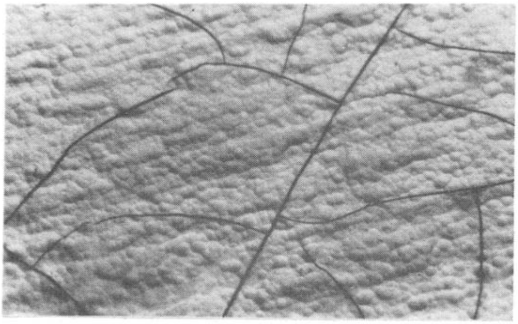

Fig. 5(2). Surface of nickel deposit obtained from the Ni(CF$_3$COO)$_2$ (20 g/l)–AlCl$_3$ (4.0 g/l)–HCON(CH$_3$)$_2$ bath at 1.0 A/dm^2 at 40°C.

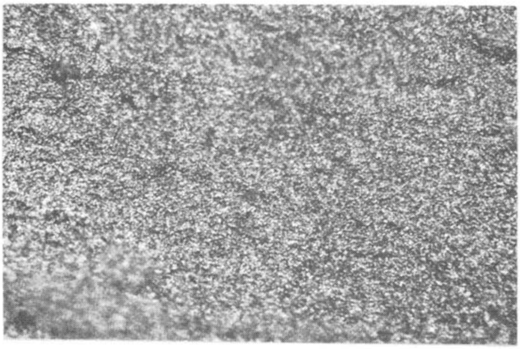

Fig. 5(3). Surface of copper deposit obtained from the Cu (CF$_3$COO)$_2$ (400 g/l)–HCONH$_2$ bath at 11.0 A/dm^2 at 50°C.

termined from this relationship.

Figure 6 shows an example of current density (log i_{oc}) – activation overvoltage (η_c) relation during the deposition of copper from the Cu(CF$_3$COO)$_2$–HCON(CH$_3$)$_2$–citric acid 200 g/l bath. The η_c value of copper deposition in the HCON(CH$_3$)$_2$ bath is very much larger (over 100 mV) than that in the HCONH$_2$ bath. The η_c values of copper deposition in those baths are smaller than that of hydrogen evolution. In Figure 6, the range in which the relation of log i_{oc}–η_c is directly linear was 1 to 3 A/dm^2 in the copper deposition from the HCON(CH$_3$)$_2$ bath. It appears that in such range of current density the Tafel's formula is valid, in other words, the charge–transfer process is rate-determining. The Tafel region for copper or nickel deposition from HCONH$_2$ and HCON(CH$_3$)$_2$ baths is shown in Table 5, and somewhat affected by the change of bath temperature and concentration of the metal trifluoroacetate.

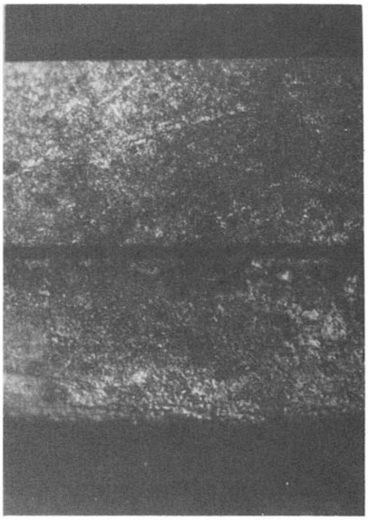

Fig. 5(4). Electrodeposited layer obtained from the Ni(CF$_3$(COO)$_2$ (100 g/l)–HCONH$_2$ bath at 1.0 A/dm^2 at 50°C.

The value of $\alpha_c n$ was determined from the slope of the Tafel line (b_c) by using (3) and shown in Table 5.

As shown in Table 5, the values of the i_{oc} of the copper and nickel depositions which was obtained by extrapolation the η_c in the relation of log i_c–η_c to 0 tended to increase with the concentration of metal

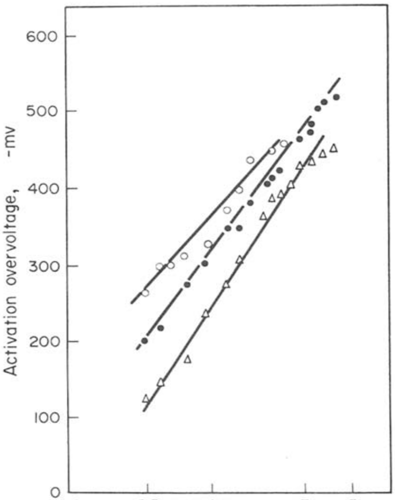

Fig. 6. Current density–activation overvoltage relation during the deposition of copper from the Cu(CF$_3$COO)$_2$ (100 g/l)–citric acid (200 g/l)–HCON(CH$_3$)$_2$ bath. Bath temp. (°C): ○: 40, ●: 50, △: 60.

Table 5. Parameter of the deposition reaction

	Bath temp. (°C)	i_{oc} (A/dm^2)	α_c	$\alpha_c n$	n	b_c (−V)	E_c (kcal/mol)	Current density of linear part (A/dm^2)
Copper deposition	30	0.54	0.72	0.49	0.7	0.12		0.7–1.5
from $Cu(CF_3COO)_2$	40	0.64	0.77	0.59	0.8	0.11	2.9	0.8–2.0
$-HCONH_2$ bath	50	0.72	0.84	0.73	0.9	0.09		0.9–3.5
Nickel deposition	50	0.040	0.52	0.62	1	0.10		0.9–2.3
from $Ni(CF_3COO)_2$	60	0.065	0.70	0.64	0.9	0.10	7.7	0.9–4.4
$-HCONH_2$ bath	70	0.080	0.76	0.70	0.9	0.09		0.9–4.8
Copper deposition	40	0.16	0.19	0.19	1	0.33		1.0–3.0
from $Cu(CF_3COO)_2$	50	0.24	0.20	0.19	0.9	0.35	8.7	1.0–3.5
citric acid	60	0.35	0.22	0.20	1	0.33		1.0–4.1
$HCON(CH_3)_2$ bath								

trifluoroacetate in the bath and the bath temperature. It was noticed that the i_{oc} of nickel deposition was smaller than that of the copper deposition in the $HCONH_2$ baths. The i_{oc} of copper deposition was smaller in $HCON(CH_3)_2$ bath than in $HCONH_2$ bath. The higher the value of i_{oc}, the easier is the depositions of the metal concerned.

The relation of log i_{oc}–log C_o is shown in Fig. 7 as a sample. In the present experiment, the relation was approximately linear. Therefore, the value of α_c was determined from the slope by using (4) and shown in Table 5. Table 5 shows α_c, $\alpha_c n$, n and b_c.

As an average of these results, the following relations were found for copper deposition:

in $HCONH_2$ bath, $\alpha_c = 0.78$,

$$n = 0.77,\ b_c = -0.113\ \text{V},$$

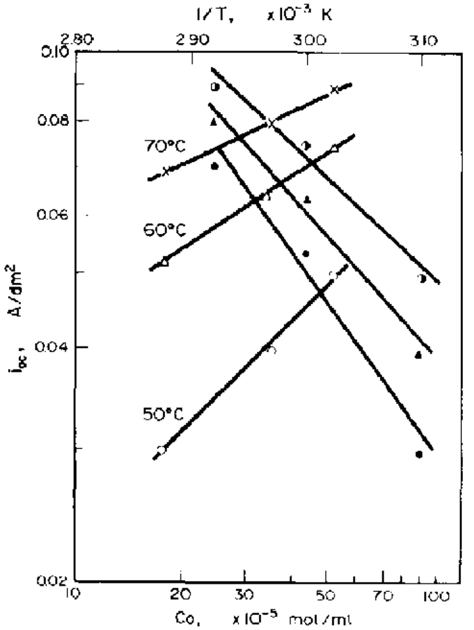

Fig. 7. Log i_{oc}–log C_o curves at various bath temperature, and log i_{oc}–$1/T$ curves at various concentration of $Ni(CF_3COO)_2$ in the $Ni(CF_3COO)_2$–$HCONH_2$ bath. $Ni(CF_3COO)_2$ ($\times 10^{-5}$ mol/ml): ◑ : 52.0, ▲ : 35.0, ● : 17.5.

in $HCON(CH_3)_2$ bath, $\alpha_c = 0.20$,

$$n = 0.96,\ b_c = -0.336\ \text{V}.$$

for nickel deposition:

in $HCONH_2$ bath, $\alpha_c = 0.66$,

$$n = 1.0,\ b_c = -0.102\ \text{V}.$$

Therefore, it may be concluded the reaction proceeds as is shown in (5) and (6) within Tafel region for copper deposition from $HCONH_2$ and $HCON(CH_3)_2$ baths and for nickel deposition from $HCONH_2$ bath.

$$M^{2+} + e^- \rightarrow M^+ \quad (5)$$

$$M^+ + e^- \rightarrow M^0 \quad (6)$$

where M is Cu or Ni.

It may also be concluded that the reaction of (5) is rate-determining, because the effect of the potential (current density) on the electrodeposition is relatively slight at low current densities, which give satisfactory deposits.

The value of E_c of copper or nickel deposition was determined from the slopes of Arrhenius curves (namely, log i_{oc}–$1/T$) shown in Fig. 7 as an example. The value of E_c was shown in Table 5.

The values of η_c, E_c and b_c in the copper electrodeposition reaction from the $Cu(CF_3COO)_2$–$HCON(CH_3)_2$–citric acid (200 g/l) bath are higher than those in the same reaction from the $Cu(CF_3COO)_2$–$HCONH_2$ bath, while the values of i_{oc} and α_c are lower, so the electrodeposition of copper from the former can be said to be more difficult.

REFERENCES

1. T. Takei, *Electrochimica Acta* **23**, 1231, 1325 (1978).
2. T. Takei, *Surface Technology* **8**, 543 (1979).