

# Electrochemical and chemical reactions in baths for plating amorphous alloys

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Deposition of amorphous alloys of (W, Co, B) is accompanied by anodic decomposition of ammonium citrate (pH 8.5) electrolyte. Products of decomposition include amines and nitro-organic compounds. Also some nitrite, and probably nitrate, is found in solutions electrolyzed for a long time. The anodic decomposition processes are catalyzed by cobalt.

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## 1. Introduction

Electrodeposition of metallic alloys on metallic surfaces requires quite different conditions from those which are usually employed for electrodeposition of a single metal. This process occurs very often with noble, very positively polarized anodes and, sometimes, with very low (even lower than 25%) current efficiency. It is usually assumed that the anode reaction is the oxidation of water to oxygen. However, under conditions existing in many electroplating baths, other oxidation processes are possible. Under conditions of low efficiency and large cell potential, the anode reactions may consume or transform components of the bath. The simplest problem is that of oxidation of metal ions [1–3], which interferes with chromium deposition from Cr(III)-containing solutions [2] and deposition of alloys, for example, from baths containing Co(II) [3]. Thus, the oxidation of metal ions is just one of many harmful oxidation reactions which may occur during electroplating.

Oxidation of other ingredients of plating solutions can sometimes lead to the formation of very toxic compounds such as HCN or I<sub>2</sub> [4]. Usually electroplating baths contain high concentrations of organic compounds necessary for complexation of cations and other organic surfactants used as brighteners and wetting agents. Many of these compounds can be oxidized in aqueous solutions at potentials less positive than the potential of oxygen evolution. For example, the carboxylic acid group can be oxidized to carbon dioxide with simultaneous production of radicals [5]. Alcohols and aldehydes can be oxidized to various products depending on substrate and oxidation conditions [6, 7]. Ammonia [8, 9], amines [9, 10], thiocyanate [11] and various other compounds frequently used in electroplating processes can also be oxidized at potentials lower than about 1.2 V with respect to the SCE. Complications following from these oxidation processes must be taken into account in the design of a plating process.

The present paper describes an investigation of the reaction sequences initiated by the anodic processes mentioned above in the specific case of an electroplating process for amorphous (W, Ni, B) or (W, Co, B) alloys [12]. The solutions used here are representative of those used in a practical plating situation, with the exception that wetting and similar agents were not employed. Detailed studies focused on the problem of oxidation of ammonia and citrate ion, which are the main “nonelectroactive” ingredients of this bath. The influence of cobalt ion on the oxidation processes was also examined.

## 2. Experimental details

For all cyclic voltammetry experiments a universal potential programmer (EG&G PARC model 175) and potentiostat (EG&G PARC model 273 or 173A) were used. Current-potential curves were either recorded with an X–Y recorder (Houston Instruments model 200) or were taken into a computer (PDP 8/e) through an ADC. A Pine MSR rotor was used in experiments with the rotating electrode. Working electrodes included a commercial Pine AFMD 19PT platinum disc electrode 0.5 cm in diameter, a BAS MF 2013 platinum electrode 0.16 cm in diameter, and a hanging mercury drop electrode (HMDE) of the Kemula and Kublik type [13]. The working platinum electrodes were polished before use with CarbiMet paper discs of decreasing grit size and subsequently with Microcloth polishing cloth with suspensions of alumina powders down to 0.05  $\mu\text{m}$ . Just before each experiment, the platinum electrodes were conditioned by alternate cathodic and anodic polarization in 1 M H<sub>2</sub>SO<sub>4</sub> until the typical cyclic voltammetric curve was obtained [14]. The reference electrode was saturated calomel (SCE) and all potentials are quoted with respect to this. A three electrode system with a large area platinum counterelectrode was used in all voltammetric experiments.

Spectrophotometric measurements were performed

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with a u.v.-visible spectrophotometer (Shimadzu model UV 260). Magnetic resonance spectra were acquired with a Varian VXR-400 multinuclear 400 MHz FT-NMR. Reference was by substitution.

All solutions were prepared from analytical grade reagents and distilled water passed through a four-cartridge Millipore Milli-Q purification system. All experiments were performed at  $25 \pm 0.5^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1. Preliminary experiments

Citrate solutions buffered with ammonia changed colour after extended electrolysis at 1.8–2 V (current density about  $20\text{ mA cm}^{-2}$ ). After 48 h of electrolysis the initially colourless solution was intensely yellow or yellow-brown and smelled of hydroxylamine or amines. These changes occurred in six nominally identical experiments in which the initial solution was 0.25 M citric acid neutralized to pH 8.5 with concentrated ammonia. During 48 h of electrolysis, the pH of the samples decreased by as much as 2 units. Also the absorbance in the visible range increased. These changes were not identical for all samples. The use of different anodes of possibly different surface state and irreproducible stirring of the solution probably contributed to differences in the final composition after electrolysis. Table 1 shows the range of results. The magnitude of these changes was significantly larger when cobalt(II) was present. Experiments performed in a cell where the anode was separated from the cathode showed that these changes in aroma and colour correspond to the anodic process.

Metal species such as Ag(II), Mn(III), Ce(IV) or Co(III) are strong oxidants used for oxidation of organic compounds [15–19]. Cobalt(III), which is one of the most powerful oxidizers, has been used on a laboratory scale for oxidation of many kinds of organic compounds, for example carboxylic acids [17]. Recently, the cobalt(III) ion has been proposed as a mediator in technological processes [18, 19]. Of course, these species exhibit the highest oxidation potentials in acidic solutions, whereas here the pH value should be held at 8.5–9 by the buffering action of citric acid/citrate and  $\text{NH}_4^+/\text{NH}_3$ . However, the pH

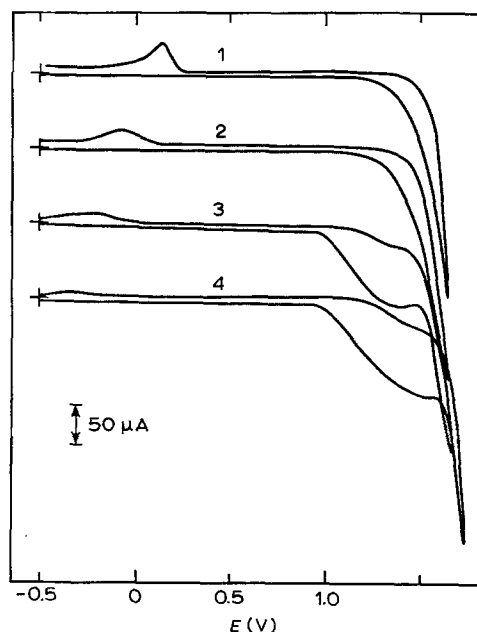


Fig. 1. Cyclic voltammety of solutions of (1)  $\text{Na}_2\text{SO}_4$ , (2)  $\text{Na}_3\text{cit}$ , (3)  $(\text{NH}_4)_2\text{SO}_4$ , and (4)  $(\text{NH}_4)_3\text{cit}$ . Salt concentration: 0.25 M, pH adjusted to 8.6 with NaOH ((1) and (2)) or with  $\text{NH}_3$  ((3) and (4)). Scan rate:  $50\text{ mV s}^{-1}$ ; Pt-disc electrode: 0.16 cm diam.

around the anode decreases at high current densities due to anodic oxidation of water.

Oxygen evolution at  $20\text{ mA cm}^{-2}$  for 1 s liberates  $2 \times 10^{-7}\text{ mol cm}^{-2}$  of hydrogen ion. This can increase the mean formal value of the hydrogen ion concentration in a 1 mm layer of the solution adjoining the anode by  $2 \times 10^{-3}\text{ M}$ . An electrolysis of only 400 s would be sufficient to neutralize the citrate ion present in this volume. Diffusion and convection make the actual situation much more complicated. A pH value of 3 is sufficient for decomposing ammonia and citrate complexes of cobalt and for producing Co(III) species, which can oxidize organic compounds present in this region. Cobalt(III) thus reduced to Co(II) can be anodically reoxidized, because the anode potential is positive enough for oxidation of even uncomplexed forms of Co(II). This situation can be described as the catalytic oxidation of ammonia and citric acid. In the present work the evidence for such behavior was sought. (Low pH values may also initiate the irreversible precipitation of tungstates or heteropolytungstates.)

Table 1. Changes of pH and absorbance during electrolysis of plating bath

Time of electrolysis (h)	pH	$w^\ddagger$	$A^\ddagger$ (600 nm)	$w^\ddagger$	$A^\ddagger$ (400 nm)	$w^\ddagger$
	w/o*		w/o*		w/o*	
0	8.6–8.6	8.6	0	0.026	0	0.01
2	8.0–7.9	6.7	0–0.004	0.031	0.03–0.05	0.09
6	7.9–7.8	6.6	0.006–0.012	0.028	0.06–0.09	0.12
12	7.9–7.7	6.7	0.014–0.024	0.028	0.11–0.16	0.23
24	7.4–6.8	6.6	0.028–0.038	0.032	0.18–0.23	0.31
48	7.3–6.7	6.3	0.042–0.054	0.035	0.28–0.32	0.46

\* 0.25 M citric acid neutralized to pH 8.6 with ammonia, range of six replicates.

† In addition 0.025 M in Co(II).

‡ Path length 1.00 cm.

Voltammetric oxidation of solutions of citrate and ammonia yielded the results of Fig. 1. Consider curves 1 and 2. In sodium citrate solution, oxidation starts at potentials about 30 mV less positive than in the supporting electrolyte, but, especially at higher current densities, the potential dependence is weaker. The well shaped cathodic peak on curve 1 at about 0.2 V corresponds to the reduction of the oxygen evolved at positive potentials. Comparison of height, potential and shape of this peak obtained in various solutions gives additional information about the anodic process occurring in the range 1.4–1.6 V. The charge corresponding to the oxygen reduction peak depends on the amount of oxygen evolved at positive potentials. The shape and the peak potential depend on the condition of the platinum surface after oxidation. Addition of sodium citrate shifts and decreases the height of the oxygen reduction peak (Fig. 1, curve 2). Total charge, measured by integration of the area under the peak, decreases by only about 30%. Thus, even in the presence of sodium citrate, the main anodic process is oxygen evolution, and oxidation of citrate occurs, under these experimental conditions, only to a limited extent. This conclusion agrees well with the observations concerning the anodic current.

The influence of ammonia on the anodic process is illustrated in curves 3 and 4 of Fig. 1. The current at potentials about 200 mV less positive than the potential of oxygen evolution we attribute to the oxidation of ammonia. Oxidation of ammonia at a platinum anode has been observed, but complex mixtures of products are formed [8, 9]. Electrode potential, current density, supporting electrolyte and, perhaps, other conditions determine whether the main product is hydrazine, hydroxylamine, nitrogen or even nitrate [8, 9]. The ratio of oxidation currents observed on curves 3 and 4 of Fig. 1 at about 1.4 V is about 2:3, as expected due to the 2:3 ratio of concentrations of ammonia.

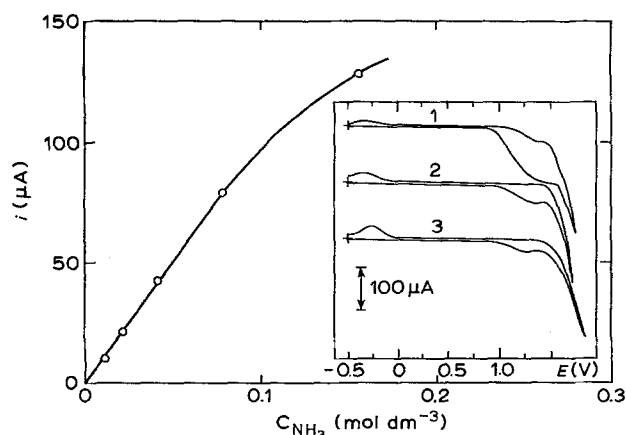


Fig. 2. Dependence of voltammetric maximum current on concentration of ammonia. Concentration of ammonia changed by dilution of ammonia buffer at constant pH. Starting conditions: 0.25 M  $(\text{NH}_4)_2\text{SO}_4$  buffered to pH 8.9 with concentrated  $\text{NH}_3$  ( $[\text{NH}_3] = 0.25 \text{ M}$ ). Inset: cyclic voltammograms obtained in ammonia buffer solutions of pH 8.9 (1) without dilution, (2) dilution 1:4, (3) dilution 1:8. Scan rate  $50 \text{ mV s}^{-1}$ , Pt-disc electrode 0.16 cm diam.

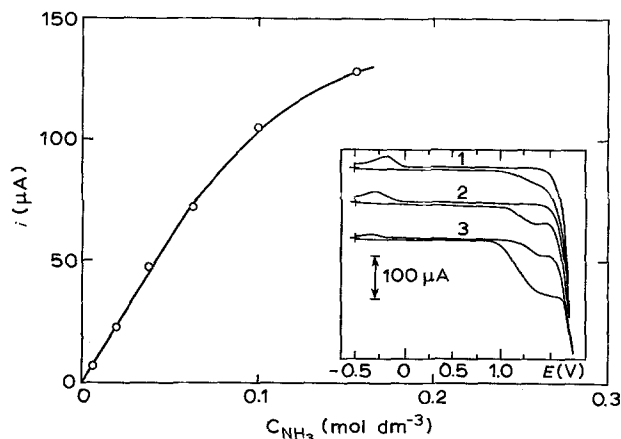


Fig. 3. Dependence of maximum current on concentration of ammonia. Concentration of ammonia was changed by adding concentrated ammonia to 0.25 M  $(\text{NH}_4)_2\text{SO}_4$ . Free ammonia concentration was calculated from the measured pH. Cyclic voltammograms obtained in 0.25 M  $(\text{NH}_4)_2\text{SO}_4$  with pH (1) 8, (2) 8.5, (3) 8.9. Scan rate:  $50 \text{ mV s}^{-1}$ ; Pt-disc electrode 0.16 cm diam.

For curves 3 and 4, the cathodic peaks have less than 20% of the charge for the peak on curve 1. The substantial negative shift of the cathodic peak may be caused by adsorption of the products of oxidation of ammonia or the ammonia-citrate mixture on the electrode surface, or by involvement of a cathodic reaction other than the reduction of oxygen.

These preliminary experiments show that oxidation of ammonia is the second most important (after oxygen evolution) anodic process. To confirm this conclusion a series of experiments was done in ammonia buffers of different concentration and pH. The results are presented in Figs 2 and 3. The ammonia concentration was changed by dilution at constant pH (Fig. 2) and by changing pH (Fig. 3). The magnitude of the anodic current which appears before oxygen evolution is proportional to the concentration of ammonia at lower concentrations.

### 3.2. Cobalt-containing baths

Cobalt compounds are known to catalyze anodic processes such as the electrooxidation of ketones [19] and the electrochemical chlorination of butadiene [20]. On the other hand, addition of cobalt salts to nickel compounds in Ni-Cd batteries increases the overpotential for oxygen evolution [21]. Thus the addition of a cobalt salt to an electroplating bath in which an inert platinum anode is used should result in faster decomposition of carboxylic acids and ammonia. Figure 4 shows voltammetric curves obtained in an ammonia buffer with free ammonia concentration of about 6 mM. The addition of a small amount of cobalt(II) shifts the oxidation to less positive potentials and improves the shape of the curves, but does not change the height of the limiting current obtained with the rotating electrode.

The results of several experiments involving ammonia oxidation with different concentrations of  $\text{CoSO}_4$  are presented in Fig. 5, which shows the dependence of oxidation current on ammonia con-

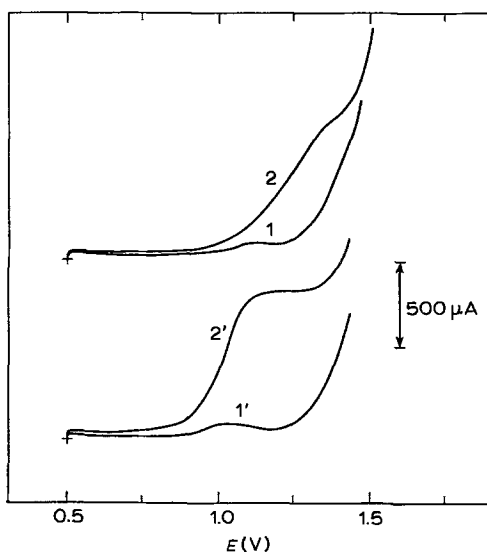


Fig. 4. Linear scan voltammetry of 0.25 M  $K_2SO_4$  + 0.05 M  $(NH_4)_2SO_4$  adjusted to pH 8.5 with ammonia ( $[NH_3] = 6.3$  mM). Curves 1, 1': stationary electrode; curves 2, 2': electrode rotated at 1000 r.p.m. Solutions for curves 1', 2' are in addition 20  $\mu$ M in  $CoSO_4$ . Scan rate: 50  $mV s^{-1}$ ; Pt-disc 0.5 cm diam.

centration for four concentrations of  $CoSO_4$ . In the linear range of the log-log plot the slope is unity, thus the current is directly proportional to ammonia concentration. The linear range depends on the concentration of  $Co(II)$ . The concentration ratio,  $(NH_3)/(Co(II))$ , at which the proportionality constant between current and concentration of ammonia begins to decrease is about 1300. Within the linear range, the proportionality constant is independent of concentration of  $Co(II)$ . For experiments with  $3 \leq (Co(II))/mM \leq 60$ , the limiting current decreases slightly with increasing concentration of cobalt, and the half-wave potential decreases about 60 mV per decade increase in concentration. The limiting cur-

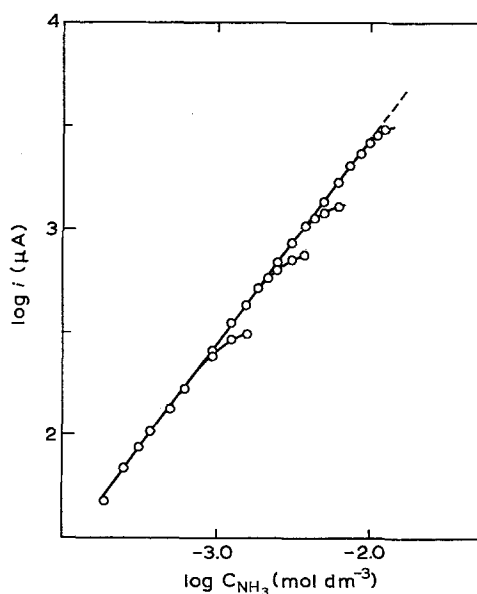


Fig. 5. Dependence of oxidation current at +1.15 V on concentration of ammonia. Solutions 0.25 M  $K_2SO_4$  +  $NH_3/(NH_4)_2SO_4$  buffer (pH 8.5) with increasing ammonia concentration and  $CoSO_4$  concentration 1, 2.5, 5, 12.5  $\mu$ M;  $E = +1.15$  V; rotating platinum electrode, rotation rate: 3000 r.p.m. diameter: 0.5 cm.

rents obtained at the RDE under these conditions fit the Levich equation. Assuming a one-electron oxidation, the limiting current yields the value  $2.1 \times 10^{-5} cm^2 s^{-1}$  for the diffusion coefficient of ammonia. The value  $2.3 \times 10^{-5} cm^2 s^{-1}$  has been reported for 1 M  $NH_3$  in water [22]. We return to discussion of this reaction below.

Preparative electrolysis was performed in stirred solution under conditions similar to those of the electroplating system. A large area platinum gauze or platinum wire anodes were used. The cathode was separated using a sintered glass frit, to avoid reduction of  $Co(II)$  at the cathode.

The first series of experiments was performed in a solution containing only  $CoSO_4$  and ammonia buffer (pH 8.5,  $(NH_3) = 6.3$  mM). Electrolysis was carried out at 0.6 and 1.1 V against SCE. At 0.6 V, the oxidation current decreased rapidly to zero. Extending the duration of electrolysis, even up to six hours, did not increase the anodic charge. The anodic charge measured in several experiments carried out at this potential (0.6 V) was many times lower than that required for oxidation of the amount of  $Co(II)$  present (40 ml of 0.1 M solution). The amount of charge depended approximately linearly on the surface area of the anode. This suggests that the reaction was stopped by poisoning of the electrode surface. A spectrophotometric examination of the solution electrolyzed at 0.6 V failed to detect  $Co(III)$ . However, a small decrease in the absorbance due to  $Co(II)$  suggested limited oxidation of  $Co(II)$  to form an insoluble compound of  $Co(III)$ . A deposit was visible on the anode surface, but no other precipitate could be seen. A slightly increased absorbance in the u.v., in the range 200–250 nm, suggests the formation of traces of an oxidation product of ammonia.

Electrolysis at 1.15 V in the same solution yielded large and persistent oxidation currents. The concentration of  $Co(II)$  decreased rapidly during the first 15 min of electrolysis to 55% of its initial value. Simultaneously the color of the anode turned from metallic platinum through yellow-brown and brown to almost black. No absorbance corresponding to a dissolved  $Co(III)$  species was observed. Longer electrolysis, up to 2 h, did not lead to significant changes in concentration of  $Co(II)$  or evidence of  $Co(III)$ . However absorbance in the u.v., close to 200 nm, increased rapidly with electrolysis time. The total charge passed during the experiment was 120 C, enough to oxidize about four times more  $Co(II)$  to  $Co(III)$ , than was present initially. The brown-black precipitate on the platinum surface was insoluble in water and in dilute sulphuric or nitric acid, but was easily removed mechanically.

Experiments similar to those described above, but with solutions containing in addition 5%  $(NH_4)_3cit$  gave similar results. A six hour electrolysis at 0.6 V gave only 19% higher charge value than a blank performed in 0.25 M  $K_2SO_4$  solution. An increase of oxidation current was observed when the anode potential was shifted to more positive values. However, after 6 h

of electrolysis at 1.15 V requiring 58 C of charge, the anode surface was clean and bright and the concentration of Co(II) was unchanged. Absorption increased significantly in the u.v. region, in proportion to the anodic charge, and poorly shaped absorption bands appeared at wavelengths between that of the Co(II) absorption and the i.r. range. As found in other experiments, such changes in visible and u.v. spectra are typical for oxidation of solutions with mixtures of citric acid and ammonia.

Recent work by Horkans *et al.* demonstrated fast decarboxylation of citrate in the presence of cobalt salts [23]. The reaction occurs only in oxygen-containing solutions, and its rate is limited by the rate of oxygen diffusion. This suggests that Co(III), which is unstable, acts as an electron-withdrawing mediator in the oxidation of the carboxylic group by molecular oxygen. Horkans *et al.* give no information about the formal potential of the Co(II)/Co(III) couple in this solution, but it must be lower than the potential of the  $O_2/O_2^{2-}$  system and positive enough to oxidize the carboxyl group to  $CO_2$ . There are analogies between this homogeneous reaction and the heterogeneous reaction described here.

### 3.3. Identification of products of bath decomposition

The solutions resulting from long time electrolysis (similar to those of a real electroplating process) were examined by visible, u.v. and NMR ( $^{14}N$ ) spectroscopy and by voltammetry. Our objectives were to (a) identify the oxidation products, and (b) investigate changes in cobalt oxidation state. All experiments described in this section were performed in 100 mL cells with copper cathode ( $A = 4.5 \text{ cm}^2$ ) and platinum anode ( $A = 2 \text{ cm}^2$ ). The solutions contained initially 5%  $(NH_4)_3\text{cit}$  and 0.5%  $CoSO_4(w/w)$ , with pH adjusted to 8.5 with concentrated ammonia. These concentrations of Co(II) and complexing agents (citrate and ammonia) are comparable with those of a commercial bath. Other components normally present (for example, sodium tungstate, boron phosphate), which probably do not influence significantly anodic processes during electroplating, were omitted. Electrolysis was carried out with constant 35  $\text{mA cm}^{-2}$  cathodic and 79  $\text{mA cm}^{-2}$  anodic current density, with and without a sintered glass frit separating the anode and cathode compartments. Solutions were not deaerated. Solutions were monitored frequently by u.v.-visible absorption and cyclic voltammetry. Changes in absorption in the visible range and NMR spectra were measured in solutions without dilution, whereas for measurements in the u.v.-region and the voltammetric experiments solutions were diluted.

Figure 6 shows u.v. spectra recorded during the electroplating process carried out in an unseparated cell. The sharp peak at 205 nm of curve 1 (before electrolysis) corresponds to absorption by carboxylate groups of citric acid. With increasing duration of electrolysis this absorption peak increases in amplitude (Fig. 6, curves 2–5), the position of maximal

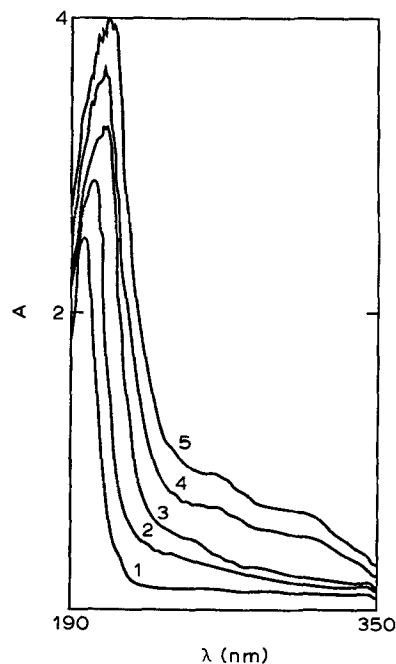


Fig. 6. Absorption spectra of 5%  $(NH_4)_3\text{cit}$  and 0.5%  $CoSO_4$  taken during 72 h electrolysis. Sampling time (h): (1) 0, (2) 2, (3) 6, (4) 36, (5) 72. Constant current,  $20 \text{ mA cm}^{-2}$ ; electrodes: cathode (Cu)  $4.5 \text{ cm}^2$ , anode (Pt)  $2 \text{ cm}^2$ ; initial pH adjusted to 8.5 with concentrated ammonia; solutions diluted 1 : 50 before analysis.

absorption shifts to longer wavelength, and the spectrum depends less on pH. After 72 h of electrolysis, the absorption maximum is almost twice as large as that of the solution before electrolysis, shifted to 215 nm, and almost insensitive to pH. This result suggests that prolonged electrolysis consumes the carboxylic groups of citric acid. The increased absorbance in the 190–220 nm region is probably due to a very highly absorbing moiety such as  $>C=C<$  or  $-N=N-$ , or perhaps to amides formed by reaction with the radical,  $NH_2\cdot$ . Compounds containing  $-N=N-$  or  $>C=C<$  groups can be produced as side products of homogeneous reactions of radicals produced at the electrode surface [5–7, 10].

These baths also display increased u.v. absorption in the region 270–280 nm (Fig. 6). This band corresponds to the  $-NO_2$  or  $-ONO_2$  group. Taking into account that the molar absorptivity for this  $n-\pi^*$  transition is relatively low ( $10\text{--}20 \text{ M}^{-1} \text{ cm}^{-1}$ ), the concentration of those compounds in the undiluted solution may be as large as 0.1 M. Increased absorption also occurs in the region close to 300 and 650 nm. This may be due to  $-NO$ .

Spectra at longer wavelengths and voltammograms for similar solutions are displayed in Fig. 7. Decrease in absorbance with time around 500 nm is caused by removal of cobalt from the solution by its reduction at the cathode. There is no spectral evidence for Co(III). For longer times of electrolysis absorption increased in the region  $\lambda < 500 \text{ nm}$ , due to products of anodic oxidation of ammonia and citric acid. Increasing absorption in this region and in the u.v. was observed in both cobalt-containing and cobalt-free solutions. However, the absorption of solutions electrolyzed with cobalt present increased faster. This is consistent

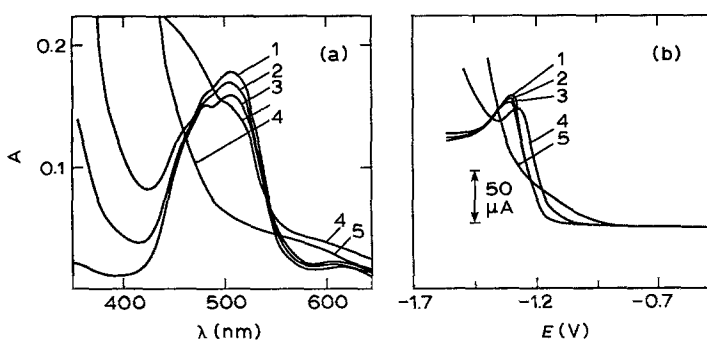


Fig. 7. Comparison of spectrophotometric (a) and voltamperometric (b) data for solution as in Fig. 6. Sampling time (h): (1) 0, (2) 2, (3) 4, (4) 12, (5) 72. Voltammograms: HMDE, 1:80 dilution in 0.5 M ammonia buffer, pH 8.5; electrode area: 0.032 cm<sup>2</sup>; scan rate: 50 mV s<sup>-1</sup>.

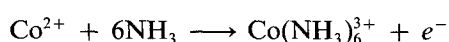
with the acceleration of this reaction in the presence of cobalt as described above.

Figure 7b presents selected voltammograms obtained using the same electroplating solution as the spectra from Fig. 7a. The decrease in peak current is due to cathodic reduction of Co(II). More subtle changes are probably due to changes in complexation of Co(II). The citrate complexes of Co(II) are rather inert and difficult to reduce [24]. The halfwave potential of Co(II)/Co(O) in noncomplexing solution is  $\sim -0.7$  V, in ammonia buffer  $-1.24$  V, and in citrate buffer  $-1.52$  V against SCE [24, 25]. As seen in Figure 7b, the cathodic limit moves to less negative potential with increasing duration of electrolysis. An aliquot of the solution after 72 h of electrolysis was added to 0.1 M NaOH and examined voltammetrically under the conditions of Figure 7b. A reduction peak at  $\sim -1.6$  V suggests the presence of hydroxylamines [26].

The u.v.-visible and voltammetric evidence is suggestive, not conclusive. More information was obtained from <sup>14</sup>N NMR spectroscopy. Before turning to this data, we conclude discussion of the catalysis of oxidation of ammonia by cobalt.

#### 3.4. Catalysis of oxidation of ammonia by cobalt

The standard potential of the Co(II)/Co(III) couple has been reported as  $+1.92$  V in acidic solution, or  $+0.17$  V in alkaline solution [27]. The potential of this system in 7 M NH<sub>3</sub>(aq) + 1 M NH<sub>4</sub>Cl was measured by Bartelt *et al.* [28]; the value of  $+0.058$  V was interpreted as the standard potential of the Co(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>/Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> couple. However, even in concentrated ammonia solutions, because of weak complexation of Co(II) by NH<sub>3</sub> (pK = 5.28), a significant fraction of Co(II) exists as other than the hexamine complex. In the case described here, Co(II)/Co(III) in 0.01 M NH<sub>3</sub>, less than 0.01% of Co(II) exists as Co(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup>. In the same solution, Co(III) should be 100% complexed (pK = 34.36). Using these values, we estimate the potential of the Co(II)/Co(III) couple, assuming that the reaction is



as  $+0.906$  V against NHE ( $+0.744$  V against SCE). This value is less positive than the waves observed in Fig. 4. Bartelt and Landazury found that even in 7 M NH<sub>3</sub> the anodic formation of Co(III) complexes produces "hydrolysis products" which precipitate on

the electrode [28]. In our case, with much lower concentrations of cobalt (as low as 10<sup>-5</sup> M) there is no evidence of a precipitate. The electrochemical and spectroscopic results taken together suggest that Co(II) is only oxidized to form a film on the electrode surface. At high concentration the film is visible, easily removed mechanically, and inhibits further oxidation of Co(II). We infer that a Co(III)-containing film is responsible for catalytic oxidation of ammonia at the anode.

#### 3.5. Identification of nitrogen-containing products by NMR

Selected NMR spectra of electrolyzed solutions are shown in Fig. 8. For the initial solution (spectrum 1) the signal at  $-356$  p.p.m. arises from the nitrogen in ammonia. Spectra 2 and 3, from solutions after 72 h of electrolysis, are slightly more complicated. Spectrum 2 is that of a solution from an unseparated cell, whereas spectrum 3 is of a solution taken from a separated anode compartment. In spectrum 3, the line at

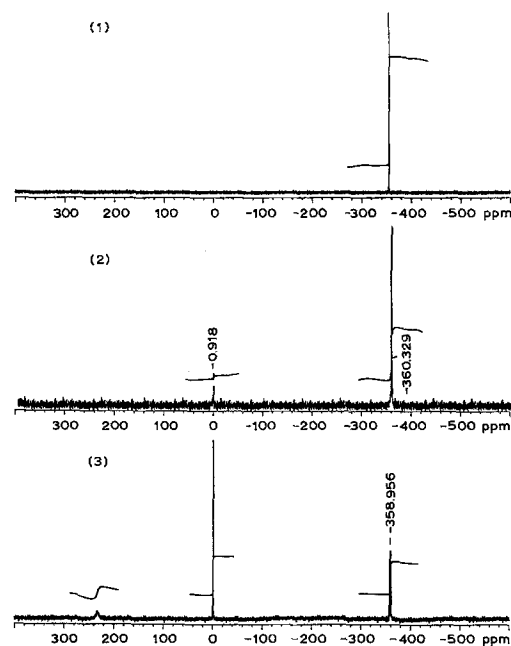


Fig. 8. NMR (<sup>14</sup>N) spectra of: (1) 5% (NH<sub>4</sub>)<sub>3</sub>cit adjusted to pH 8.5 with concentrated ammonia; (2) the same solution but 0.5% in CoSO<sub>4</sub> and after 72 h of electrolysis without separated anode and cathode compartments; (3) solution treated as 2, but taken from anodic compartment of system with the separator. All other conditions of electrolysis as for Fig. 6. Reference: CH<sub>3</sub>NO<sub>2</sub>.

– 359 p.p.m. arises from ammonia or amines, that at – 1 p.p.m. is from nitro-compounds or nitrate, and that at + 230 p.p.m. is due to nitrite, formed as an intermediate in the oxidation of nitro-compounds [29, 30]. The NMR spectrum of the solution taken from the cathodic compartment of the same experiment revealed only one signal, that for ammonia. When this solution was made alkaline and heated, the odor of ammonia was apparent, and this procedure eliminated the NMR signal (at – 359 p.p.m.). Thus only ammonia or ammonium ion nitrogen is present in the cathode compartment of the separated cell.

In spectrum 2 (of the solution from the cell with unseparated electrodes) only two peaks are seen, a more intense one at – 359 p.p.m. and a weaker one at – 1 p.p.m. It is very probable that the band at – 359 p.p.m. corresponds to amine nitrogen, because the intensity of this peak was the same after the solution was made alkaline and heated. The line at – 1 p.p.m. appears in the place characteristic for nitro-compounds. No signal corresponding to nitrite was detected.

In the cell with separated electrodes, only oxidation processes occur in the anode compartment, and nitrogen can only be oxidized. The compounds formed are stable or if not then are oxidized again. Ultimately, compounds accumulate which contain nitrogen in high oxidation states. The solubility of nitro-compounds in water is rather poor; thus the signal observed at – 1 p.p.m. may be connected not only with the nitro-group but also with nitrate, which can result from oxidation of nitro-compounds [29].

In the solution taken from the cell with unseparated electrodes multiple cycles of oxidation and reduction are possible. Because the oxidation of ammonia and carboxylic acids proceeds through intermediate radical forms, the formation of many different products is possible. These new compounds can be oxidized or reduced further. In fact, after a longer electrolysis, a steady state may be reached. The oxidizable nitrogen compounds, such as ammonia, amines and hydroxylamines, can be transformed by anodic reaction to the nitrate ion, nitro- or nitroso-compounds and molecular nitrogen. These molecules (except probably  $N_2$ ), after transport to the cathode, can be reduced back to amines, hydroxylamines or other compounds containing nitrogen in low oxidation states. These oxidation-reduction cycles are probably not symmetrical, so new compounds are formed on successive cycles of oxidation.

The NMR results confirm and clarify the previous observations that in the plating solution nitro-compounds and amines exist, and that the concentration of ammonia decreases during the plating process. The NMR experiments also demonstrate that amides are absent (no line at  $\sim$  – 260 p.p.m.). Other possible forms of nitrogen such as hydroxylamines and nitrate may be present in the solution at relatively low concentration, which are not detected by  $^{14}N$  NMR spectroscopy. (Detection limits even for com-

pounds such as ammonia which have narrow line-widths may be as high as  $10^{-2}$  M.)

Integration of the NMR signals provides some information about the relative concentration of different nitrogen compounds and about depletion of nitrogen in the bath. In the case of the cell with separated electrodes, integration of signals gave 93% of the initial concentration in the cathodic space and 90% in the anodic one. The differences of only 10% could be caused by escaping of gaseous  $NH_3$  and by formation of other nitrogen-containing compounds at concentrations below detection limits. A similar integration performed for the spectra of the solution taken from the cell with unseparated electrodes showed only 48% of the initial concentration of nitrogen. It is hard to explain this loss of more than half of the nitrogen signal by the formation of many nitrogen-containing compounds at low concentration. It is more likely that a significant amount of gaseous nitrogen is evolved under these conditions.

### 3.6. *The effect of oxidation of the bath on cathodic reduction of cobalt*

The large changes in composition of the bath described above modify the cathodic reduction of metals in the electroplating solution. Table 2 contains data collected during a 72 h experiment simulating the electroplating process. The initial concentration of  $CoSO_4$  was this time lower than in experiments reported previously, 0.2%. These data show that the process of Co(II) reduction in the system containing anode and cathode in the same solution is significantly less efficient than the reduction of Co(II) in the system consisting of separated anode and cathode compartments. In the latter case, the amount of cobalt deposited per hour is almost the same for the first 12 h. (The decrease in reduction efficiency observed after 12 h of electrodeposition was the result of depletion of Co(II)). Products formed at the anode are the most likely cause of the decrease in efficiency in the undivided cell. The oxidation products can modify Co(II) reduction in two ways. First, it is possible that the extent and nature of complexation of Co(II) is changed because of decomposition of  $NH_3$  and citrate and formation of new compounds. Secondly, the new molecules formed in the anodic reaction may decrease the rate of reduction of Co(II) by adsorbing on the cathode surface.

## 4. Conclusions

The types of processes reported here for ammonium citrate baths with or without cobalt(II) must occur quite generally for the extreme potentials required for the deposition of amorphous alloys. From the qualitative point of view, the obvious phenomena, such as colour, odour, change in efficiency, reported here occur also in plating baths of the recommended formulations [12], including solutions containing Ni(II) in place of Co(II). Furthermore other common

Table 2. Changes of cathode weight during reduction of cobalt from ammonium citrate solution.\*

Time of electrolysis (h)	pH		$\Delta m$ (mg)		Co plated (%)		Current efficiency (%)	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1	8.5	8.5	2.17	3.75	2.8	4.8	2.46	4.25
2	8.3	8.6	2.49	7.32	3.3	9.4	1.41	4.14
4	8.0	8.8	3.47	17.01	4.6	21.4	0.98	4.80
12	8.3	9.1	10.73	49.32	14.5	66.6	1.01	4.64
72	8.1	9.3	69.36	73.24	91.3	96.3	1.08	1.14

\* Initial volume: 100 ml; initial amount of  $\text{CoSO}_4$ : 200 mg.

(a) Anode and cathode in same compartment

(b) Anode compartment (0.1 M  $\text{Na}_2\text{SO}_4$ ) separated by glass frit.

components of plating baths such as ethylenediamine and triethyleneamine are oxidized anodically more easily than water under these conditions. Separating the anodic and cathodic processes during electroplating of alloys is a simple and effective method of preventing deterioration of the plating bath.

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### References

- [1] M. Chomakova and S. Vitkova, *J. Appl. Electrochem.* **16** (1986) 669.
- [2] D. J. Barclay and W. M. Morgan, Fr. Patent 2 294 250; UK Patent 1 431 693; *Chem. Abst.* **86** (1977) 179240.
- [3] A. M. A. El-Halim and R. M. Khalil, *J. Appl. Electrochem.* **17** (1987) 956.
- [4] D. J. Barclay and J. M. L. Vigar, Ger. Patent 2 943 049; *Chem. Abst.* **93** (1981) 33966.
- [5] Lj. V. Minevski and R. Radzic, *J. Appl. Electrochem.* **18** (1988) 240.
- [6] A. Capon and R. Parsons, *J. Electroanal. Chem.* **45** (1973) 205.
- [7] K. Takamura and S. Sakamoto, *ibid.* **113** (1980) 273.
- [8] H. Gerisher and A. Maurer, *ibid.* **25** (1970) 421.
- [9] 'Encyclopedia of Electrochemistry of Elements', (edited by A. J. Bard) Vol. VIII, Marcel Dekker, New York (1978), p. 411.
- [10] M. Masui, H. Sayo and Y. Tsuda, *J. Chem. Soc. (B)* (1968) 973.
- [11] D. A. Holtzen and A. S. Allen, *Anal. Chim. Acta* **69** (1974) 153.
- [12] G. A. Croopnick and D. M. Scruggs, US Patent 4 529 668, 16 July 1985.
- [13] W. Kemula and Z. Kublik, *Anal. Chim. Acta* **18** (1958) 104.
- [14] H. Angerstein-Kozłowska, B. E. Conway and W. B. A. Sharp, *J. Electroanal. Chem.* **43** (1973) 9.
- [15] M. Fleishmann, D. Pletcher and A. Rafinsky, *J. Appl. Electrochem.* **1** (1971) 1.
- [16] Sa Van Ho, *ibid.* **17** (1987) 398.
- [17] A. A. Clifford and W. A. Wathers, *J. Chem. Soc.* (1965) 2796.
- [18] A. El Ghazali, S. Belcardi and J. J. Rameou, *J. Appl. Electrochem.* **18** (1988) 27.
- [19] H. Wendt and H. Schneider, *ibid.* **16** (1986) 134.
- [20] Y. Takasu, Y. Matsuda, M. Harada and M. Masaki, *J. Electrochem. Soc.* **131** (1984) 349.
- [21] R. D. Armstrong, G. W. D. Briggs and E. A. Charles, *J. Appl. Electrochem.* **18** (1988) 215.
- [22] 'International Critical Tables V', National Academy of Sciences, Washington, DC (1979), p. 64.
- [23] J. Horkans, W. Ng, M. M. Plechaty, V. Stimming and J. B. Machlke, *J. Appl. Electrochem.* **19** (1989) 152.
- [24] E. Bednarkiewicz and Z. Kublik, *Electrochim. Acta* **24** (1979) 121.
- [25] G. S. Alberts, R. H. Wright and C. C. Parker, *J. Electrochem. Soc.* **113** (1966) 687.
- [26] 'Encyclopedia of Electrochemistry of Elements', (edited by A. J. Bard), Vol. III, Marcel Dekker, New York (1975), p. 64.
- [27] 'Standard Potentials in Aqueous Solutions', (edited by A. Bard, R. Parsons and J. Jordan), Marcel Dekker, New York (1985).
- [28] H. Bartelt and S. Landazury, *J. Electroanal. Chem.* **22** (1969) 105.
- [29] 'Encyclopedia of Electrochemistry of Elements', (edited by A. J. Bard), Vol. XIII, Marcel Dekker, New York (1979), Chapters 2 and 3.
- [30] S. Wawzonek and Tsung-Yuan Su, *J. Electrochem. Soc.* **120** (1973) 747.
- [31] J. J. Cruyvagen and I. F. J. van der Merve, *J. Chem. Soc. Dalton Trans.* (1987) 1701.
- [32] M. T. Pope, 'Heteropoly and Isopoly Oxometalates', Springer-Verlag, Berlin, (1983).