On the mechanism of electroless plating.
Part 3. Electroless copper alloys

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It has been shown that alloying copper with different metals has a pronounced effect on hydrogen evolution during anodic oxidation of formaldehyde and under electroless plating conditions. The codeposition of platinum, palladium, gold or nickel reduces the ratio between the amount of hydrogen evolved and the deposited metal. Diminishing the hydrogen evolution has a favourable effect on the structure of the deposited alloy. The reduced amount of hydrogen, as well as the synergetic effects observed during anodic oxidation of formaldehyde, can be explained by assuming a spillover of the oxidation intermediates.

1. Introduction

Electroless or autocatalytic metal deposition is a process in which reduction of metal ions and oxidation of a reducing agent simultaneously take place at a catalytic surface. The most widely used reducing agent in electroless copper solutions is formaldehyde, whose oxidation on a copper surface is accompanied by evolution of hydrogen gas [1].

$$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^-$$
$$+ 2H_2O + H_2$$
$$(1)$$
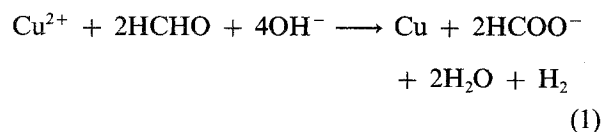
It is known that the incorporation of hydrogen into the copper layers causes brittle deposits [2]. This brittleness can be influenced by the deposition rate [3], the temperature and certain additives [4]. However, a more direct way to avoid hydrogen embrittlement would be to deposit the metal without hydrogen evolution, or at least with a reduced amount of evolved gas.

Several authors have studied the anodic oxidation of formaldehyde at metal surfaces [5-10]. At platinum and palladium the oxidation takes place without any gas evolution [5, 6].

$$HCHO + 3OH^- \xrightarrow{Pt,Pd} HCOO^- + 2H_2O + 2e^-$$
$$(2)$$
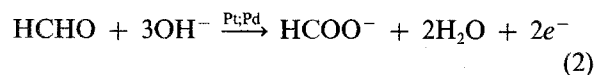
On copper one molecule of H_2 is always formed for every two molecules of formaldehyde oxidized [6].

$$2HCHO + 4OH^- \xrightarrow{Cu} 2HCOO^- + 2H_2O$$
$$+ H_2 + 2e^-$$
$$(3)$$
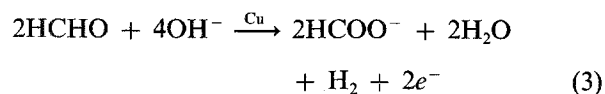
At gold and silver the amount of hydrogen is between these two limiting values, depending on the applied potential and the pH of the solution [6-8].

Enyo [11, 12] studied the anodic oxidation of formaldehyde on copper alloys and found synergetic effects, for example on copper–nickel electrodes. Although pure nickel has no catalytic activity for the oxidation of formaldehyde [6], it has an obvious influence on the catalytic properties of copper. It has been known since 1948 [13] that nickel can be codeposited from electroless copper solutions with formaldehyde as a reducing agent and that the structure of the deposit is favourably influenced.

In this study we investigated whether the anodic oxidation of formaldehyde on copper is influenced by alloying the electrode with metals such as platinum, palladium, gold or nickel. We attempted to prepare electroless solutions from which these alloys could be deposited, and we checked whether reduction of hydrogen evolution influences the quality of the deposited layers.

2. Experimental details

The investigations of the anodic oxidation of formaldehyde were performed on electrodes made from tablets of the alloy obtained by melting and mixing appropriate amounts of the two metals under reducing conditions and quenching in cold water. The tablets were rolled to a sheet about 0.5 mm thick and cut in pieces of area a few square centimeters. Segregation can cause enrichment at the surface of the metal with the lower surface energy [14], so the electrodes were polished with emery paper (Buehler Grit 600) just before each experiment. We made X-ray Photoelectron Spectroscopy (XPS) measurements with copper–platinum alloys and found that the surface platinum concentration was significantly reduced 30 min after polishing.

The anodic oxidation experiments were performed in a solution of 0.10 mol l^{-1} HCHO and 0.15 mol l^{-1} NaOH at 25($\pm$0.1)° C. A conventional electrochemical cell was used, with a large-area platinum sheet as counter electrode and a saturated calomel electrode as a reference. All potentials in this work are given with

respect to this saturated calomel electrode (SCE). The electrochemical measurements were done with a Wenking ST72 potentiostat in combination with a Wenking VSG72 voltage scan generator and a Philips PM8141 x-y recorder. Before each experiment all electrodes were polished, kept at -2.0 V (SCE) for a few minutes to remove surface oxides, and then scanned in the positive direction at a rate of 2 mV s^{-1}. When palladium or copper–palladium alloys were used, hydrogen was absorbed during the pretreatment at -2.0 V (SCE). In this case the electrodes wère kept at -1.0 V (SCE) until the anodic oxidation of the absorbed hydrogen was completed, before scanning started.

During potentiostatic oxidation of formaldehyde the amount of hydrogen was analysed with the aid of a gas burette. The consumption of formalydehyde was determined iodometrically [15] in separate experiments.

Electroless plating was performed on glass slides, roughened with silicon carbide and activated in SnCl$_2$/ HCl and PdCl$_2$/HCl solutions. To measure the ductility of the deposited metals, the layers were partially detached from the glass slides, bent through 180 degrees, pressed flat and bent backwards. One such bend over 180 degrees and back was called "1 bend".

All solutions were made up with reagent grade chemicals and deionized water.

3. Results

3.1. Anodic oxidation

We measured current–potential curves on different copper–platinum, copper–palladium, copper–gold and copper–nickel alloys, as well as on the pure metals. The curves measured on Cu$_{99}$Pt$_1$ and Cu$_{90}$Ni$_{10}$ are given as typical examples in Figs 1 and 2 respectively, together with the curves on copper, platinum and nickel. Between -1.0 and -0.9 V (SCE) the anodic oxidation of formaldehyde sets in and the rate increases with increasing potential. At about -0.6 V (SCE) a maximum is obtained on copper and on the copper alloys. At more anodic potentials the current
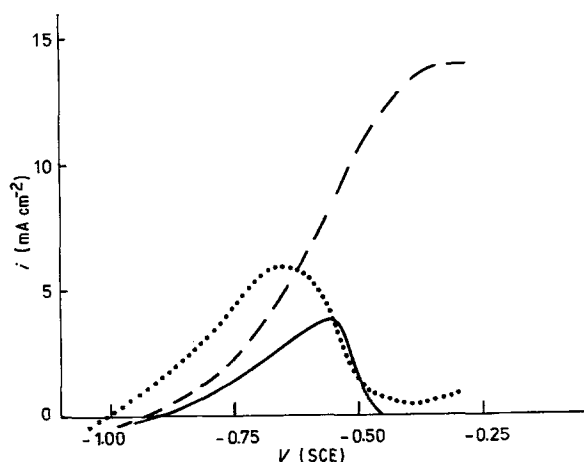
Fig. 1. Current–potential curves for copper (——), platinum (– – –) and Cu$_{99}$Pt$_1$ alloy ($\cdots$) in a solution of 0.10 mol l^{-1} HCHO + 0.15 mol l^{-1} NaOH.
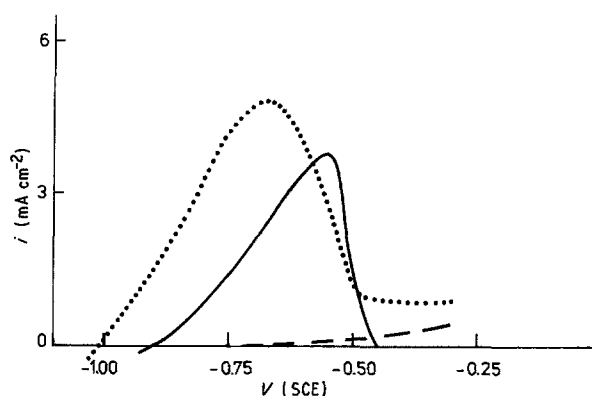
Fig. 2. Current–potential curves for copper (——), Ni (– – –) and Cu$_{90}$Ni$_{10}$ alloy ($\cdots$) in a solution of 0.10 mol l^{-1} HCHO + 0.15 mol l^{-1} NaOH.

decreases as a result of oxide formation or adsorption of oxidation products on these electrodes [16]. In all cases, the current density at the alloys was larger than on the pure metals, in the potential range from the rest potential to the current maximum. This synergetic effect was even observed on copper–nickel alloys although nickel itself shows a negligible catalytic activity for the formaldehyde oxidation. The synergetic effect was the smallest on copper–gold alloys, despite a good activity of pure gold [16].

To investigate whether the alloying of copper had an influence on the amount of hydrogen evolved, we made hydrogen analyses as a function of the charge passed under potentiostatic control. Fig. 3 shows that 2 at.% platinum in copper has a pronounced effect on the amount of hydrogen. From these analyses the percentage of the current due to Reaction 3 was obtained. Table 1 shows that on alloy electrodes this reaction is seriously reduced in comparison with pure copper. We also performed formaldehyde analyses as a function of the charge passed under potentiostatic control, at the same electrodes. This yields the percentage of the current due to Reaction 2. Assuming that formate is the final oxidation product, the two percentages should add up to 100%. At the pure metals this is the case (Table 1). With the alloys there are rather large deviations from 100%. This is caused by the fact that the hydrogen and formaldehyde analyses were performed in separate experiments. Although the electrodes were firmly polished with emery paper just before each experiment, XPS measurements showed that noticable enrichment of Cu at the surface took place during the first 30 min. As the potentiostatic experiments lasted a few hours, the surface compo-

Table 1. Percentages of the oxidation current due to Reactions 2 and 3 under potentiostatic control at -0.60 V (SCE)

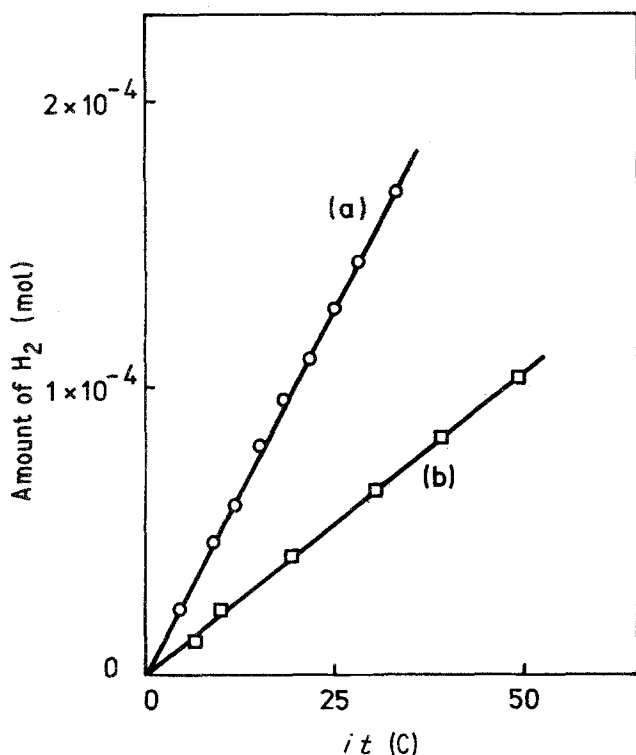| Metal	Reaction 2 (%)	Reaction 3 (%)
Cu	0	100
Cu$_{99}$Pt$_1$	68	43
Cu$_{98}$Pt$_2$	56	41
Cu$_{90}$Ni$_{10}$	24	67
Pt	100	0

Fig. 3. The amount of hydrogen evolved as a function of the charge for electrodes of (a) copper and (b) $Cu_{98}Pt_2$ in $0.10 \, mol \, l^{-1}$ HCHO + $0.15 \, mol \, l^{-1}$ NaOH at -0.60 V (SCE).
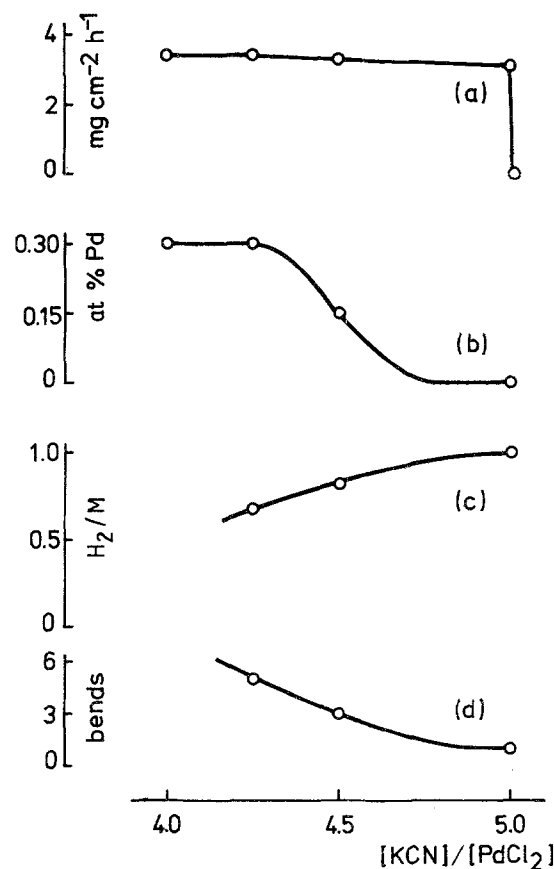

Fig. 4. (a) deposition rate, (b) percentage of codeposited palladium, (c) ratio of hydrogen and deposited metal and (d) the ductility of the deposited layer as a function of the ratio of KCN and $PdCl_2$ concentrations. Solution ($mol \, l^{-1}$): 0.08 $CuSO_4$ + 0.006 $PdCl_2$ + 0.096 EDTA (4 Na) + 0.11 NaOH + 0.10 HCHO + KCN. Temperature 50° C.

sition changed during the experiment. This is the reason for the deviations in the results. Nevertheless, it is obvious that hydrogen evolution is greatly reduced at platinum and nickel alloys in comparison with pure copper.

3.2. Electroless alloy plating

We tried to prepare electroless solutions for the deposition of copper alloys. To deposit two metals simultaneously in an alloy containing significant concentrations of each it must be possible to reduce both metal ions at the same potential at comparable rates. To achieve this goal, we tried to complex the more noble metal ions more effectively than the less noble metal ions. In that case, the equilibrium potentials of the two metals approach each other and simultaneous reduction can be expected. A nice example of such an electroless alloy plating is known from the literature. Molenaar [17] used ethylenediaminetetraacetic acid (EDTA) to complex Cu^{2+} ions and CN^- for the Au^+ ions. Alloys with a copper/gold ranging from 0 to 1 could be obtained. He also made hydrogen analyses during electroless deposition [18] and found a ratio between the amount of H_2 evolved and the deposited metal of 0.90 at $Cu_{26}Au_{74}$ alloys. When the amount of gold in the deposited layers was increased to 98.5% the ratio decreased to 0.71.

In a similar manner, we tried to prepare stable electroless copper/palladium solutions. It turned out that the ratio of the CN^- and Pd^{2+} concentrations played a decisive role in determining the properties of these solutions. Two complexes are known for the

Pd^{2+}/CN^- system [19]: $Pd(CN)_4^{2-}$ and $Pd(CN)_5^{3-}$. The solutions were unstable when the ratio of KCN and $PdCl_2$ concentrations in the electroless solutions was lower than 4. Metal became homogeneously deposited immediately after the addition of the formaldehyde. When the ratio was higher than 5, the solutions were completely stable, but deposition did not occur on activated surfaces either. Apparently, the excess CN^- poisons the catalytic surface. The results of a solution of $0.08 \, mol \, l^{-1}$ $CuSO_4$, $0.006 \, mol \, l^{-1}$ $PdCl_2$, $0.096 \, mol \, l^{-1}$ EDTA (4 Na-salt), $0.11 \, mol \, l^{-1}$ NaOH, $0.10 \, mol \, l^{-1}$ HCHO and KCN concentration between 0.024 and $0.030 \, mol \, l^{-1}$ are shown in Fig. 4. The experiments were performed at 50° C. The deposition rate was not influenced by the KCN concentration (Fig. 4a). The stability of the solutions at 50° C increased as the KCN concentration increased. At a ratio of 4 the solutions did not show any homogeneous reaction during about 1 h. With a ratio of 5 the solutions remained stable for more than 2 h. It is obvious, from Fig. 4b that palladium can be codeposited with ratios lower than 5. As palladium is incorporated into the layers the amount of H_2 decreases (Fig. 4c). As little as 0.3 at % palladium reduces the H_2 amount by about 30%. Fig. 4d shows that the ductility of the deposited layers (number of bends before the $10 \, \mu m$ layers crack) clearly increased as the amount of H_2 decreases.

Table 2. Composition and plating results of two electroless Cu–Ni solutions

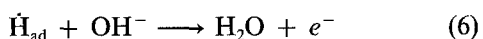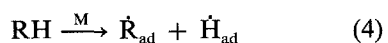|	I	II
$CuSO_4$ $(mol\,l^{-1})$	0.02	0.02
$NiSO_4$ $(mol\,l^{-1})$	8×10^{-4}	4×10^{-4}
TEA[1] $(mol\,l^{-1})$	0.065	
TIPA[2] $(mol\,l^{-1})$		0.065
NaOH $(mol\,l^{-1})$	0.20	0.20
HCHO $(mol\,l^{-1})$	0.10	0.10
Temperature (°C)	25	45
plating rate $(mg\,cm^{-2}\,h^{-1})$	1.0	1.9
at % Ni	3.8	1.5
H_2/M	0.67	0.47
Ductility (bends)	1	3

[1] TEA = triethanolamine
[2] TIPA = triisopropanolamine

As nickel is less noble than copper, we tried to make up electroless copper/nickel solutions with complexing agents that complex Cu^{2+} ions better than Ni^{2+} ions. We found that triethanolamine (TEA) and triisopropanolamine (TIPA) met this condition. With both compounds copper/nickel solutions could be prepared which yielded coherent, adherent and ductile metal layers. Table 2 gives the composition of two solutions, together with the results obtained. When $NiSO_4$ was omitted from these solutions, the deposited copper was powdery, brittle and non-adherent. Table 2 shows that the amount of hydrogen evolved is clearly diminished when nickel is codeposited. The stability of these solutions was good for the duration of the experiments. When oxygen was passed through the solutions they were stabilized completely and could be operated for several days [20].

4. Discussion

The results show that incorporation of small amount of palladium, platinum, gold and nickel into a copper layer has a pronounced effect on the oxidation of formaldehyde, both under potentiostatic conditions and in electroless plating solutions. It is obvious that the alloys catalyse the oxidation better than the separate metals, and that the rate of hydrogen evolution at these alloys is much lower than on pure copper. In earlier work [6, 21] we proposed the following general scheme for the anodic oxidation of reducing agents in electroless plating solutions

$$RH \xrightarrow{M} \dot{R}_{ad} + \dot{H}_{ad} \qquad (4)$$

$$\dot{R}_{ad} + OH^- \longrightarrow ROH + e^- \qquad (5)$$

$$\dot{H}_{ad} + OH^- \longrightarrow H_2O + e^- \qquad (6)$$

$$2\dot{H}_{ad} \longrightarrow H_2 \qquad (7)$$

In this scheme RH represents the reducing agent. In the case of formaldehyde this stands for CH_2OHO^-, the methylene glycol anion, which is the main constituent in alkaline formaldehyde solutions [15]. Reaction 4 is the dehydrogenation of the reducing agent,

Table 3. Apparent exchange current density (i^0) for the reversible hydrogen reaction and heat of hydrogen adsorption (ΔH) at different metals

Metal	$\log i^0$ $(mA\,cm^{-2})$	ΔH $(kJ\,mol^{-1})$
Cu	-9.7	-108
Ni	-8.4	-119
Au	-8.4	-110
Pt	-6.4	-140
Pd	-5.7	-112

catalysed by the metal, M, at which the process takes place. Apparently, nickel does not have sufficient activity for this step in the case of formaldehyde, as oxidation is negligible on pure nickel. Reaction 5 represents the oxidation of the adsorbed intermediate and yields the final oxidation product formate ions. Reaction 6 competes with Reaction 7 for the adsorbed hydrogen. When Reaction 6 dominates, Reaction 2 will be the overall process, while Reaction 7 results in overall Reaction 3.

In analogy with earlier work [6] we can calculate the rates (v) of Reactions 6 and 7 at different metals

$$v_6 = \frac{i^0 \exp(\alpha F\eta/RT)}{F}$$

$$v_7 = k\theta^2 \exp(\Delta H/RT)$$

in which i^0 is the apparent exchange current density, α is the transfer coefficient (≈ 0.5) and η is the over-potential for the reversible hydrogen reaction. For Reaction 7 the rate constant, k, is $5 \times 10^{15}\,mol\,cm^{-2}\,s^{-1}$, while ΔH represents the heat of hydrogen adsorption and θ is the hydrogen coverage. F, R and T are the Faraday constant, the gas constant and the absolute temperature respectively. The relative rates of Reactions 6 and 7 determine the fractions of the anodic oxidation of formaldehyde due to the overall Reactions 2 and 3. For the alloys, the percentage, P, of Reaction 3 can be estimated as follows

$$P = \frac{xv_7^M + (1-x)v_7^{Cu}}{xv_6^M + (1-x)v_6^{Cu} + xv_7^M + (1-x)v_7^{Cu}} 100\%$$

in which the fraction of metal M in the copper alloy is given by x. We assume that the coverage of hydrogen is uniform over the alloy surface, due to a spillover of this adsorbed species. Spillover of adsorbed hydrogen is well known, especially at group VIII metals [22]. We have calculated the percentage of Reaction 3 taking extreme values of θ (0.01 and 1.0) and the values of i^0 and ΔH from Table 3. Table 4 compares these values with the experimental values obtained during anodic oxidation and in electroless plating solutions. It is obvious that the experimental results lie between the calculated values in each case. So the mechanism in combination with the kinetic rate laws for v_6 and v_7 for pure metals can be used to give a reasonable description of the hydrogen economy during formaldehyde oxidation at copper alloys.

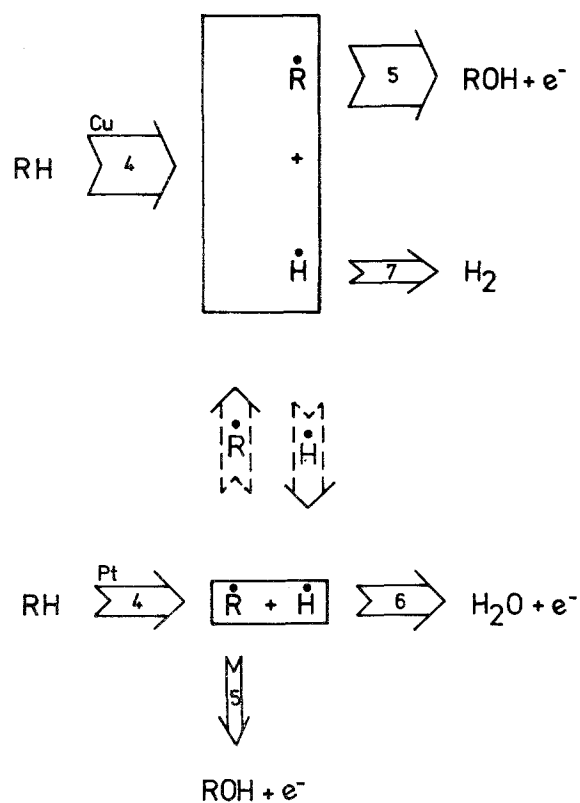In the previous calculations the two alloy metals are

Fig. 5. Schematic representation of the reactions occurring at a Cu–Pt alloy. The thickness of the arrows represents the relative rates; the numbers refer to Reactions (4)–(7).

treated as independent materials. The catalytic activity of each metal is considered to be unaffected by the other metal: only hydrogen can be spilled over from one metal to the other. Although the synergetic effect observed at the alloys seems to contradict this assumption, this effect can be explained when a spillover of the $\dot{R}$ intermediates is also assumed. Buck and Griffith [5] have shown that Reaction 5 is the rate determining

step in the anodic formaldehyde oxidation at platinum. Comparing calculations of the rate of Reaction 7 with the current densities measured at copper shows that this reaction is very probably the rate determining step at this metal. When a spillover of both $\dot{R}$ and $\dot{H}$ can take place, the reaction at platinum will be enhanced by diffusion of $\dot{R}$ to copper, while the rate at copper will be increased by diffusion of $\dot{H}$ to platinum. This process is schematically shown in Fig. 5. A similar spillover effect must occur on the other copper alloys. Even for nickel, on which Reaction 4 does not take place, a synergetic effect can be explained as long as the rate of Reaction 7 at copper plus the rate of hydrogen spillover to nickel is lower than the rate of Reaction 4 or Reaction 5 at the surface copper atoms. When the nickel content is increased, Reaction 4 or Reaction 5 becomes rate determining and synergism will diminish. Enyo [12] indeed found that the highest activity is observed at $Cu_{89}Ni_{11}$ alloys.

In conclusion, we can say that the mechanism for the anodic oxidation of formaldehyde proposed in [6] can explain the results obtained at copper alloys. Both the synergetic effect and the reduced hydrogen evolution can be understood, assuming a spillover of the oxidation intermediates. Codeposition of small amounts of palladium, platinum or nickel reduces the hydrogen evolution during electroless plating, as expected. A diminished hydrogen production has a favourable influence on the structure of the deposited layers.

Acknowledgement

Table 4. Calculated and experimental percentages of the formaldehyde oxidation due to Reaction 3, during anodic oxidation or electroless plating

Electrode material	Potential of anodic oxidation V (SCE)	Percentage Reaction 3		
		Calculated		Experimental
		$\theta = 0.01$	$\theta = 1.0$	
Cu	−0.60	90	100	100
$Cu_{99}Pt_1$	−0.60	24	100	43
$Cu_{98}Pt_2$	−0.60	14	100	41
Pt	−0.60	0	0	0
$Cu_{90}Ni_{10}$	−0.60	51	100	67
Deposited metal	**Mixed Potential V (SCE)**			
$Cu_{99.85}Pd_{0.15}$	−0.72	81	100	82
$Cu_{99.7}Pd_{0.3}$	−0.71	66	100	69
[1]$Cu_{26}Au_{74}$	−0.52	7	100	90
[1]$Cu_{1.5}Au_{98.5}$	−0.47	1	100	71
[2]Cu	−0.70	100	100	100

[1] Results from [18]
[2] Results from [23]

References

[1] R. M. Lukes, *Plating* **51** (1964) 1066.

[2] Y. Okinaka and S. Nakahara, *J. Electrochem. Soc.* **123** (1976) 475.

[3] C. J. G. F. Janssen, H. Jonker and A. Molenaar, *Plating* **58** (1971) 42.

[4] A. Molenaar, J. E. A. M. van den Meerakker and J. Boven, *Plating* **61** (1974) 649.

[5] P. Buck and L. R. Griffith, *J. Electrochem. Soc.* **109** (1962) 1005.

[6] J. E. A. M. van den Meerakker, *J. Appl. Electrochem.* **11** (1981) 387.

[7] R. M. van Effen and D. H. Evans, *J. Electroanal. Chem.* **103** (1979) 383.

[8] M. Beltowska-Brzinzka, *Electrochim. Acta* **30** (1985) 1193.

[9] P. M. Bindra and J. Roldan, *J. Electrochem. Soc.* **132** (1985) 2581.

[10] I. Ohno, O. Wakabayashi and S. Haruyama, *J. Electrochem. Soc.* **132** (1985) 2323.

[11] M. Enyo, *Bull. Chem. Soc. Jpn* **58** (1985) 2043.

[12] M. Enyo, *J. Electroanal. Chem.* **201** (1986) 47.

[13] S. Wein, *Metal Finishing* **46** (**8**) (1948) 58.

[14] M. J. Sparnaay and G. E. Thomas, *Surf. Sci.* **135** (1983) 184.

[15] J. F. Walker, 'Formaldehyde', 3rd Edn (Reinhold, New York, 1964).

[16] S. Haruyama and I. Ohno, 'Electroless Deposition of Metals and Alloys', edited by M. Paunovic and I. Ohno, Proc. Vol. 88-12, (The Electrochem. Soc., Inc. Pennington, New Jersey, 1988) pp. 23, 29, 31, 33.

[17] A. Molenaar, *J. Electrochem. Soc.* **129** (1982) 1917.

[18] A. Molenaar and B. C. Meenderink, *J. Electrochem. Soc.* **132** (1985) 574.

[19] R. M. Smith and A. E. Martell, 'Critical Stability Constants', Vol 4 (Plenum, New York, 1976).

[20] E. Scholtens, private communications.

[21] J. E. A. M. van den Meerakker, *J. Appl. Electrochem.* **11** (1981) 395.

[22] W. Curtis Conner Jr, in 'Advances in Catalysis', Vol 34, edited by D. D. Eley, H. Pines and P. B. Weisz (Academic Press, New York, 1986).

[23] J. E. A. M. van den Meerakker, *Thin Solid Films* **173** (1989) 139.