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Kinetics of electroless copper deposition using cobalt(II)-ethylenediamine complex compounds as reducing agents

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Abstract

Electroless copper deposition using Co(II)-ethylenediamine (*En*) complexes as reducing agents was investigated in 0.4–1.2 M *En* solutions at 50 and 70 °C. There is a complicated dependence of the process rate on pH, *En* concentration and temperature. A copper deposition rate up to 6 μm h^{-1} (50–70 °C) in relatively stable solutions (pH $\sim$ 6) can be achieved. The stoichiometry of the Cu(II) reduction at pH 6–7 corresponds to the reaction:

$$\mathrm{Cu}En_2^{2+} + 2\ \mathrm{Co}En_2^{2+} \xrightarrow{\mathrm{Cu}} \mathrm{Cu} + 2\ \mathrm{Co}En_3^{3+}$$

The correlation between the rate of the copper deposition on the catalytic surface and the concentration of the $\mathrm{Co}En_2^{2+}$ complex species in the solution was found.

1. Introduction

Electroless copper plating solutions are widely used for the formation of copper layers on plastics and other dielectrics during the production of printed circuits and for the decorative metallizing of plastics etc. [1–5]. The conventional alkaline electroless copper plating solutions contain a Cu(II) salt, a reducing agent (usually formaldehyde), complexing agents which prevent the precipitation of Cu(II) hydroxide and various additives which improve the properties of the coatings obtained and/or protect from copper(II) reduction in the solution bulk.

The drawbacks of the conventional electroless copper plating solutions are related to environmental and technological problems: (i) formaldehyde and many copper(II) ligands are environmentally unacceptable; (ii) copper plating rate and solution stability are not always high enough; and (iii) the plating bath can not be recycled (i.e., the reducing agent (formaldehyde) oxidizes irreversibly).

A new type reducing agent for electroless metal plating processes, cobalt(II) complexes with amines, was recently proposed [6–8]. Co(II) complexes with ethylenediamine (*En*) are used for copper deposition, and they can be regenerated after the plating process by reducing the reaction product, cobalt(III), to the initial state. Co(III) reduction can be carried out both chemically and electrochemically [8].

The thermodynamic aspects of the Cu(II) reduction by Co(II) in ethylenediamine solutions (redox potentials, process equilibria) were discussed in [8]. The calculations have shown that Co(II) is thermodynamically able to reduce Cu(II) to the metallic state in aqueous ethylenediamine (0.4–1.2 M) solutions at pH over 3.6–3.9. Experimentally the autocatalytic reduction of copper(II) ions by Co(II)–*En* complex was observed at pH > 5.5–5.8 (at 50 °C).

The process of autocatalytic reduction of Cu(II) by Co(II) in *En* solutions and the partial reactions of the overall process – cobalt(II) anodic oxidation and copper(II) cathodic reduction – were studied by electrochemical quartz crystal microgravimetry [9–11]. The conclusion was drawn that $\mathrm{Co}En_3^{2+}$ is the electrochemically active species in Cu(II) reduction process.

The aim of this work was to investigate the influence of pH, temperature and ethylenediamine concentration on the Cu deposition rate from novel electroless copper plating solutions.

2. Experimental details

2.1. *Solutions*

Analytical grade chemicals and distilled water were used to prepare the solutions. The electroless copper plating solution contained (M): $\mathrm{CuCl_2}$ 0.05; $\mathrm{CoCl_2}$ 0.15;

ethylenediamine (*En*) 0.4, 0.6 or 1.2; pH 5–11. The pH was adjusted using hydrochloric acid. The pH was measured at 50 and 70 °C using an EV-74 pH meter with a high-temperature glass electrode ESL 63-07 (Belarus). The calibration of the pH meter provided a measurement accuracy of ±0.01 pH unit. The electroless copper plating solutions were prepared as follows: the necessary amounts of water, $CuCl_2$ solution, hydrochloric acid and $CoCl_2$ solution were mixed in a reaction vessel, oxygen was removed from the solution by bubbling Ar, and the required volume of *En* solution was added.

2.2. *Electroless copper deposition*

The substrate was a Pt sheet (2.0 cm × 2.5 cm) electroplated with Cu for 15 min from acid copper solution (0.2 M $CuSO_4$ + 0.5 M H_2SO_4) at 1.5 A dm^{-2}. Before the electroless plating the copper surface was activated for 10 s in an acid $PdCl_2$ solution (1 g L^{-1}). Electroless deposition experiments were carried out in a closed thermostated glass vessel of 90 ml volume containing 73 ml of the plating solution; Ar was constantly passed through the working solution. The experiments were carried out at 50 and 70 °C, and the loading was 1.4 dm^2 L^{-1}. The Cu electrode potential was measured using a voltmeter M 202M (Belarus) against an $Ag/AgCl/KCl_{sat}$ reference electrode. All potentials are presented with reference to the SHE.

2.3. *Analytical procedures*

The copper deposited on the surface to be plated was determined by weighing. Cu(II) and Co(II) concentrations in the solution were determined titrimetrically according to [12, 13]. The change in solution volume during electroless plating due to the evaporation of water at elevated temperature was estimated experimentally (1.3 ml within 30 min at 50 °C, and 1.95 ml within 30 min at 70 °C).

3. Results and discussion

3.1. *Electroless copper deposition at 50 °C*

The behaviour of the Cu–Cu(II)–Co(II)–*En* system in weakly acidic chloride-containing solutions depends very strongly on pH and, to a smaller extent, on the ethylenediamine concentration (in the range of 0.4–1.2 M). The experiments showed (Table 1) rather easy transition from chemical Cu dissolution at lower pH values to Cu deposition as a result of autocatalytic reduction of Cu(II) ions at higher pH. The pH range of this transition from one process to another is relatively narrow, only 0.05–0.10 pH unit (Table 1).

The dissolution of copper is related, apparently, to the presence of the chloride ions in the solution and the formation of Cu(I)-chloride complex compounds:

Table 1. Effect of pH and ethylenediamine (*En*) concentration on Cu deposition
Solution composition (M): $CuCl_2$ 0.05, $CoCl_2$ 0.15, *En*. 50 °C; immersion time 2 h.

En/M	pH	Cu/mg
0.4	5.72	−3.4
	5.77	+1.2
0.6	5.58	−7.9
	5.63	+2.7
1.2	5.37	−1.9
	5.47	+9.6

$$Cu^{2+} + Cu \xrightarrow{Cl^-} 2\ Cu^+ \tag{1}$$

This explanation is supported by the fact that copper dissolution is not observed in the chloride-free nitrate or sulphate solutions. The process (Equation 1) is possible in the case where the cobalt(II) oxidation reaction

$$CoEn_n^{2+} + (3-n)En \xrightarrow{Cl^-} CoEn_3^{3+} + e^- \tag{2}$$

does not shift the Cu potential to more negative values corresponding to copper ion reduction to metal. The calculated redox potential of Co(III)–Co(II) couple in *En* solutions becomes more negative with increase in pH [8]. When this potential on the Cu electrode reaches the potential of copper ion reduction to Cu, the autocatalytic deposition of copper becomes possible.

The lowest pH at which Cu(II) reduction by Co(II) occurs, decreases with increase in *En* concentration (Table 1). This corresponds to more negative reversible Co(III)–Co(II) redox potentials at higher *En* concentrations.

Both the amount of copper deposited on the surface to be plated (catalytic surface) and the total copper(II) reduced (including Cu(II) reduced in the solution bulk) depend on pH and *En* concentration (Figures 1 and 2). The amount of copper deposited on the catalytic surface is very sensitive to pH and the pH dependence has a distinct maximum at about 6.0–6.1. Up to this maximum practically all the copper formed is deposited on the surface (i.e., the plating solution is stable). At higher pH the total amount of copper(II) reduced increases further and reaches a maximum at pH 6.4–6.7. But in these conditions the copper formed in solution represents the larger part of all Cu(II) reduced. The higher the *En* concentrations the higher the copper plating and total Cu(II) reduction rates achieved; this *En* effect is more distinct when the *En* concentration increases from 0.4 to 0.6 M.

After comparing the results obtained with data for Co(II) distribution among the complexes with ethylenediamine [8], it is obvious that the plating process begins when the $CoEn_2^{2+}$ species appears in the solution, and it is possible to conclude that not only $CoEn_3^{2+}$ but also $CoEn_2^{2+}$ species is electroactive in the catalytic reaction at low pH. This point of view is supported by the similar

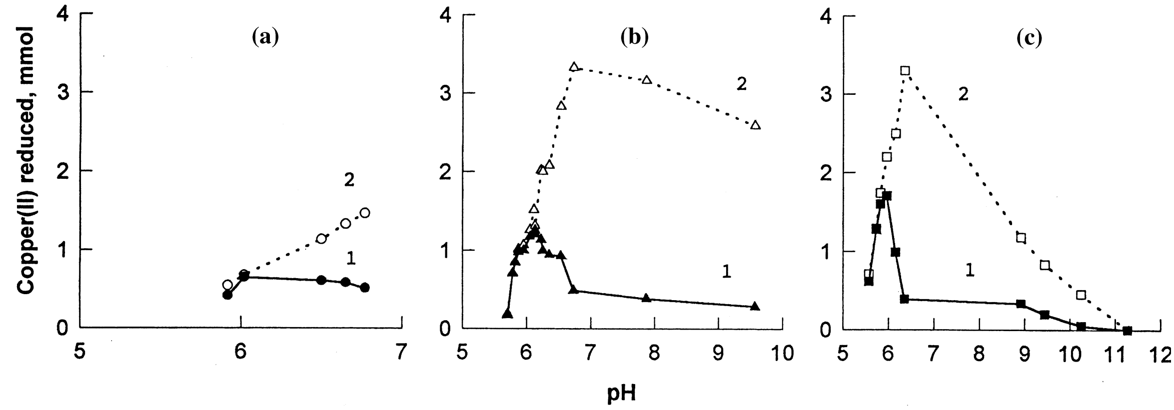

Fig. 1. Dependence of the copper deposited on the surface to be plated (black marks) and of total amount of the Cu(II) reduced (white marks) on pH at 50 °C. Solution composition (M): $CuCl_2$ 0.05, $CoCl_2$ 0.15; *En*: (a) 0.4, (b) 0.6, (c) 1.2. Plating time 2 h.

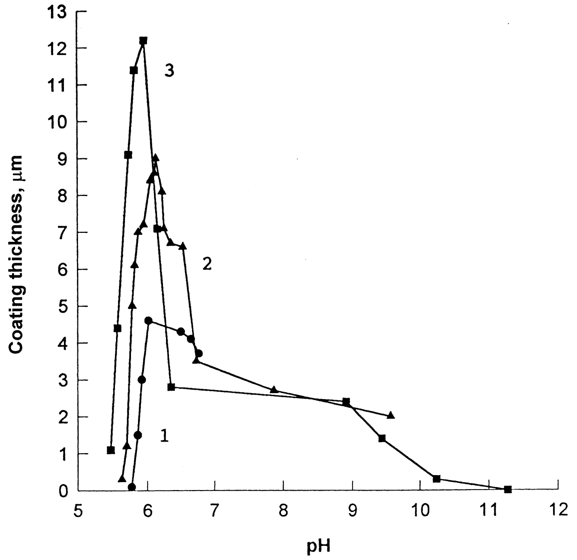

Fig. 2. Dependence of the copper coating thickness on pH. Solution composition (M): $CuCl_2$ 0.05; $CoCl_2$ 0.15; *En*: (1) 0.4, (2) 0.6, (3) 1.2. 50 °C. Plating time 2 h.

shape of the pH dependence of total amount of copper(II) reduced (curve 2 on Figure 1(a)), and of $\mathrm{Co}En_2^{2+}$ complex concentration [8]. It should be noted that the $\mathrm{Co}En_3^{2+}$ species is absent in 0.4 M *En* solutions and it is less probable that they take part in the Cu(II) reduction process. On the one hand, the $\mathrm{Co}En_3^{2+}$ complex was concluded to be an electroactive species in the anodic oxidation of Co(II) on noble metal electrodes in *En* solutions [14, 15], as well as on copper [9–11]. On the other hand, it is known that in homogeneous reactions, for example, in Co(II) oxidation by oxygen in *En* solutions, $\mathrm{Co}En_2^{2+}$ [16], or both $\mathrm{Co}En_2^{2+}$ and $\mathrm{Co}En_3^{2+}$ [17] take part. In our case the reacting species are probably Co(II) complexes with both 2 and 3 *En*.

The largest amounts of copper are reduced (nearly all Cu(II) present in the solution) (Figure 1(b)–(c), curves 2) at pH values when the $\mathrm{Co}En_2^{2+}$ complex predominates in solution. Therefore, the stoichiometry of the Cu(II) reduction reaction at lower pH (up to pH 7) can be expressed as follows:

$$\mathrm{Cu}En_2^{2+} + 2\,\mathrm{Co}En_2^{2+} \xrightarrow{\mathrm{Cu}} \mathrm{Cu} + 2\,\mathrm{Co}En_3^{3+} \tag{3}$$

As may be seen from Reaction 3, no free ethylenediamine appears additionally during the reduction process, thus the pH should not change. This was confirmed by pH measurements during the plating process which showed that pH remained constant under the conditions investigated.

The pH at the surface of the coating (pH_s) was also measured. The pH_s was measured using an ordinary glass electrode, the surface of which was in the reaction zone [18, 19]. The bulb of the glass electrode was covered with a thin nylon net which was preactivated by $PdCl_2$. A thin copper layer was then deposited from the electroless plating bath. Then the glass electrode with the net was immersed into the electroless copper plating solution and the copper deposition began. The pH_s values measured during one hour remained exactly constant for solutions of pH under 7.

At higher pH, when $\mathrm{Co}En_3^{2+}$ predominates, the reaction rate is much lower. The stoichiometry of the Cu(II) reduction reaction at pH > 7 can be expressed as follows:

$$\mathrm{Cu}En_2^{2+} + 2\,\mathrm{Co}En_3^{2+} \xrightarrow{\mathrm{Cu}} \mathrm{Cu} + 2\,\mathrm{Co}En_3^{3+} + 2\,En \tag{4}$$

The free ethylenediamine is formed in Reaction 4, and the pH should increase due to *En* protonation:

$$En + \mathrm{H}^+ \rightleftharpoons En\mathrm{H}^+ \tag{5}$$

pH measurements showed an increase in pH during the Cu(II) reduction process in accordance with the stoichiometry of Reaction 4. For example, during the reduction process (2 h) the pH increased from 7.87 to 8.39 in the solution containing 0.6 M *En*, and from 7.97 to 8.42 in the solution containing 1.2 M *En*.

The decrease in the total amount of copper(II) reduced with increase in pH after reaching the maximum value can be related to the decrease in $\mathrm{Co}En_2^{2+}$ complex concentration. In 0.6 M *En* solution the process rate decrease is not so great (Figure 1(b)), and up to 10% of Co(II) remains in the form of $\mathrm{Co}En_2^{2+}$ complex at the highest possible pH values [8]. In 1.2 mol $\mathrm{l^{-1}}$ *En* solution Cu(II) reduction slows considerably at pH 9–10 and comes to a stop at pH > 11 (Figure 1(c)). The distribution of Co(II) among the complexes shows that the concentration of $\mathrm{Co}En_2^{2+}$ complex decreases to 2–0.1% at pH 9–10, and this complex disappears at pH ~ 11. On the other hand, the decrease in the total amount of copper reduced can, to some extent, be attributed to the decrease in the potential difference between Co(III)–Co(II) and Cu(II)–Cu redox couples at pH over 7, especially in 1.2 M *En* solution where this difference becomes more positive by 130 mV [8].

The time dependencies of the total amount of copper reduced show a considerable influence of pH and ethylenediamine concentration on the kinetics of copper deposition (Figure 3). The Cu(II) reduction rate rises with increase in pH in 0.4 mol $\mathrm{l^{-1}}$ *En* solution. The form of the time dependences of the Cu(II) reduced shows that the rate decreases with time (Figure 3(a)).

When *En* concentration increases to 0.6 M, the Cu(II) reduction rate increases about twofold as compared with that at the same conditions in 0.4 M *En* solution (cf. Figure 3(a) and (b)). The form of the time dependencies of Cu(II) reduced changes at pH > 6.6, when the greater part of Cu(II) is reduced during the first 30 min (Figure 3(b), curves 7–10); this may be explained by the increased reduction of Cu(II) in the solution bulk.

The kinetics of Cu(II) reduction in 1.2 M *En* solution is similar to that in 0.6 M *En* solution, except for the considerable decrease in the reduction rate at higher pH (Figure 3(c)).

The measurements of the open-circuit copper potential during the plating process (mixed potential E_m) showed the shift of the E_m to more negative values with increase in pH up to 6.7 in 0.4 M *En* solutions and up to pH 8–9 in 0.6 and 1.2 M *En* solutions. With further increase in pH the E_m remains almost constant or becomes a little more negative. Comparison of the measured E_m values with the calculated equilibrium potential of the copper electrode (E_{eq}) in the *En* solutions investigated [8], and with the results of the kinetic investigations (Figures 1 and 2) shows that the copper(II) reduction localized on the catalytic surface occurs at a relatively small overpotential; the difference between E_m and E_{eq} is in the range from −5 to −30 mV. The considerable copper(II) reduction in the solution bulk occurs when the overpotential reaches −(50–100) mV. The copper potential is equal to E_{eq} at pH over 11 (1.2 M *En* solution), and this is in agreement with the experimental data which show the absence of Cu(II) reduction under these conditions (Figure 1(c)).

As the process of copper deposition is very sensitive to pH changes the additional experiments were carried out using buffering systems. Two kinds of buffer solutions were used: a citrate buffer (pH 6.0) and acetate buffers (pH 6.0 and 6.2) [20]. The electroless copper solutions were prepared using these buffer solutions instead of water. The results show that the employment of citrate or acetate buffer solution diminishes the rate of copper deposition on the catalytic surface more than twofold (Figure 4) and insignificantly decreases the total amount of copper reduced.

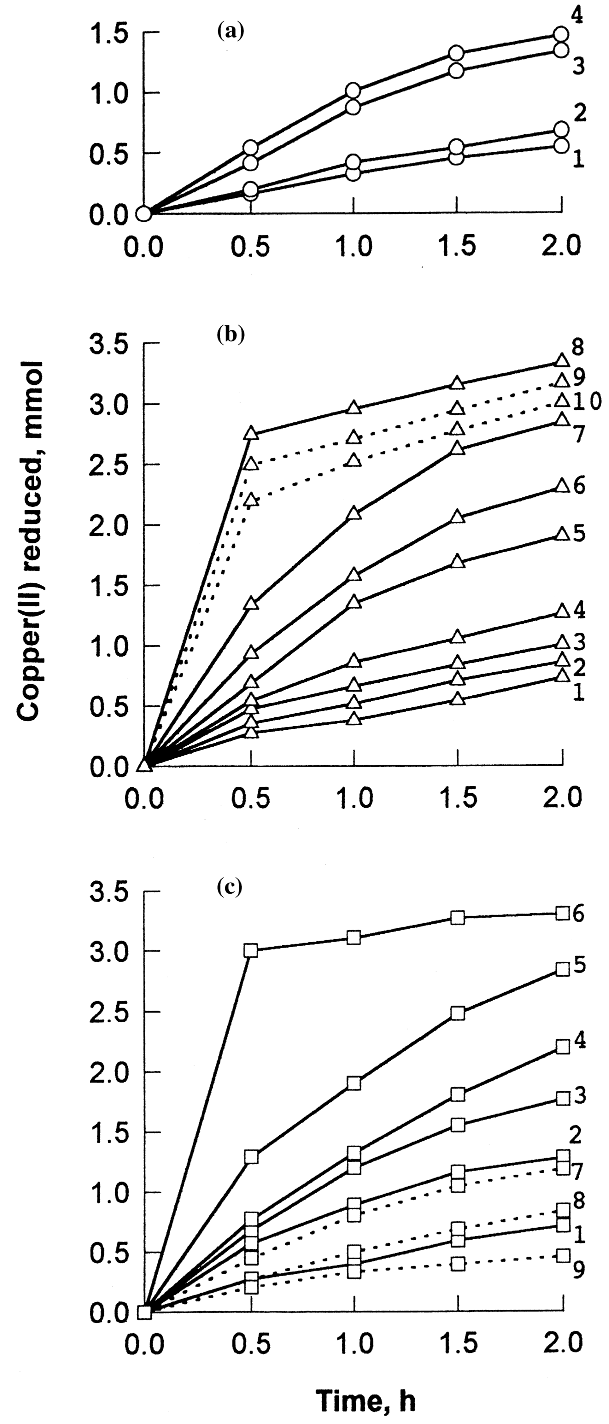

Fig. 3. Time dependence of the total amount of Cu(II) reduced at 50 °C. Solution composition (M): $\mathrm{CuCl_2}$ 0.05, $\mathrm{CoCl_2}$ 0.15; *En*: (a) 0.4, (b) 0.6, (c) 1.2. pH (a): (1) 5.92, (2) 6.02, (3) 6.65, (4) 6.74; (b): (1) 5.78, (2) 5.82, (3) 5.95, (4) 6.05, (5) 6.22, (6) 6.35, (7) 6.53, (8) 6.73, (9) 7.87, (10) 9.57; (c): (1) 5.57, (2) 5.73, (3) 5.82, (4) 5.96, (5) 6.15, (6) 6.35, (7) 8.91, (8) 9.44, (9) 10.24.

The effect of the widely used reducing agent, sodium hypophosphite ($\mathrm{NaH_2PO_2}$), on the copper(II) reduction

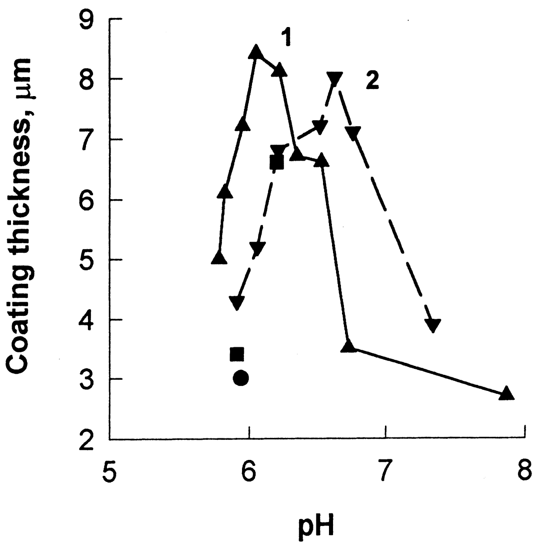

Fig. 4. Dependence of the copper coating thickness on pH. Solution composition (M): $CuCl_2$ 0.05, $CoCl_2$ 0.15, *En* 0.6; additives: none (▲), NaH_2PO_2 0.05 (▼), citrate buffer solution (●), acetate buffer solution (■). Temperature 50 °C. Plating time 2 h.

by cobalt(II) was also tested. The hypophosphite addition shifts the pH region of the effective copper plating to higher values by about 0.5 pH unit (Figure 4) and increases the solution stability in the pH range 6.2–6.8.

The addition of buffer solutions or sodium hypophosphite practically did not change E_m, that is, the balance of two partial reactions (copper(II) reduction and cobalt(II) oxidation) in the presence of additives remained unchanged whereas the overall process rate and, consequently, the partial reactions rate did change.

3.2. *Electroless copper deposition at 70 °C*

The dependencies of copper coating thickness on pH at 70 °C are of the same type as at 50 °C (cf. Figures 5 and 2), but coatings of higher thickness can be deposited in 0.4 and 0.6 M *En* solutions while in 1.2 M *En* solution the maximum coating thickness is of the same order (Table 2).

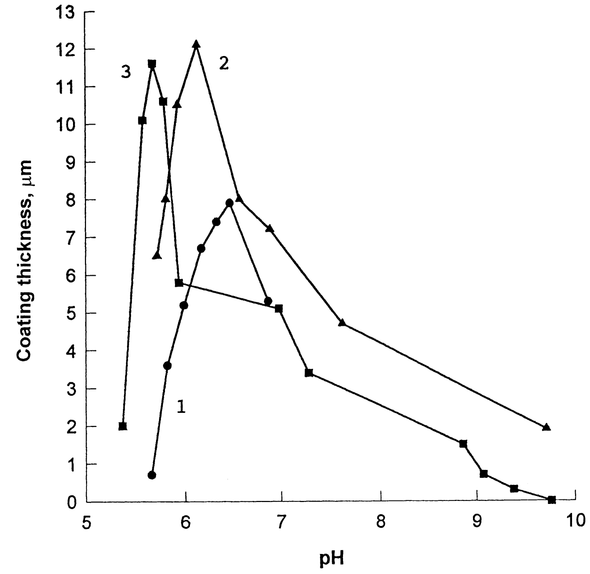

Fig. 5. Dependence of the copper coating thickness on pH. Solution composition (M): $CuCl_2$ 0.05, $CoCl_2$ 0.15; *En*: (1) 0.4, (2) 0.6, (3) 1.2. Temperature 70 °C. Plating time 2 h.

Table 2. Maximum average copper deposition rate on the catalytic surface at 50 and 70 °C
Solution composition (M): $CuCl_2$ 0.05, $CoCl_2$ 0.15, ethylenediamine.

En /M	50 °C		70 °C	
	pH	Copper deposited /µm h^{-1}	pH	Copper deposited /µm h^{-1}
0.4	6.02	2.3	6.47	4.0
0.6	6.13	4.5	6.13	6.1
1.2	5.96	6.1	5.68	5.8

The dependencies of the copper deposited on the catalytic surface and of the total amount of copper(II) reduced (including Cu(II) reduced in the solution bulk) on pH and *En* concentration at 70 °C demonstrate the same copper deposition process sensitivity to pH (Figure 6) as at 50 °C. However, two differences referring to the solution stability can be found when

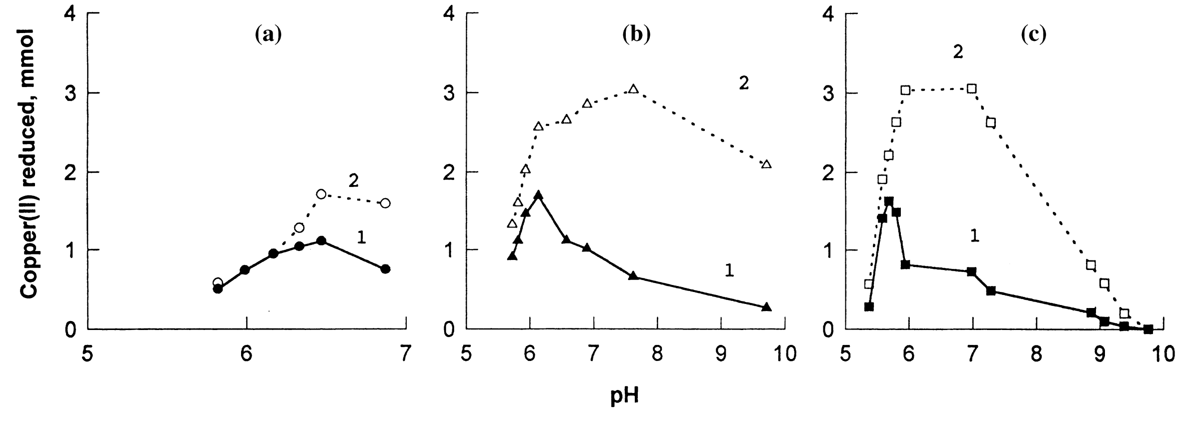

Fig. 6. Dependence of the copper deposited on the surface to be plated (black marks) and of total amount of the Cu(II) reduced (white marks) on pH at 70 °C. Solution composition (M): $CuCl_2$ 0.05, $CoCl_2$ 0.15; *En*: (a) 0.4, (b) 0.6, (c) 1.2. Plating time 2 h.

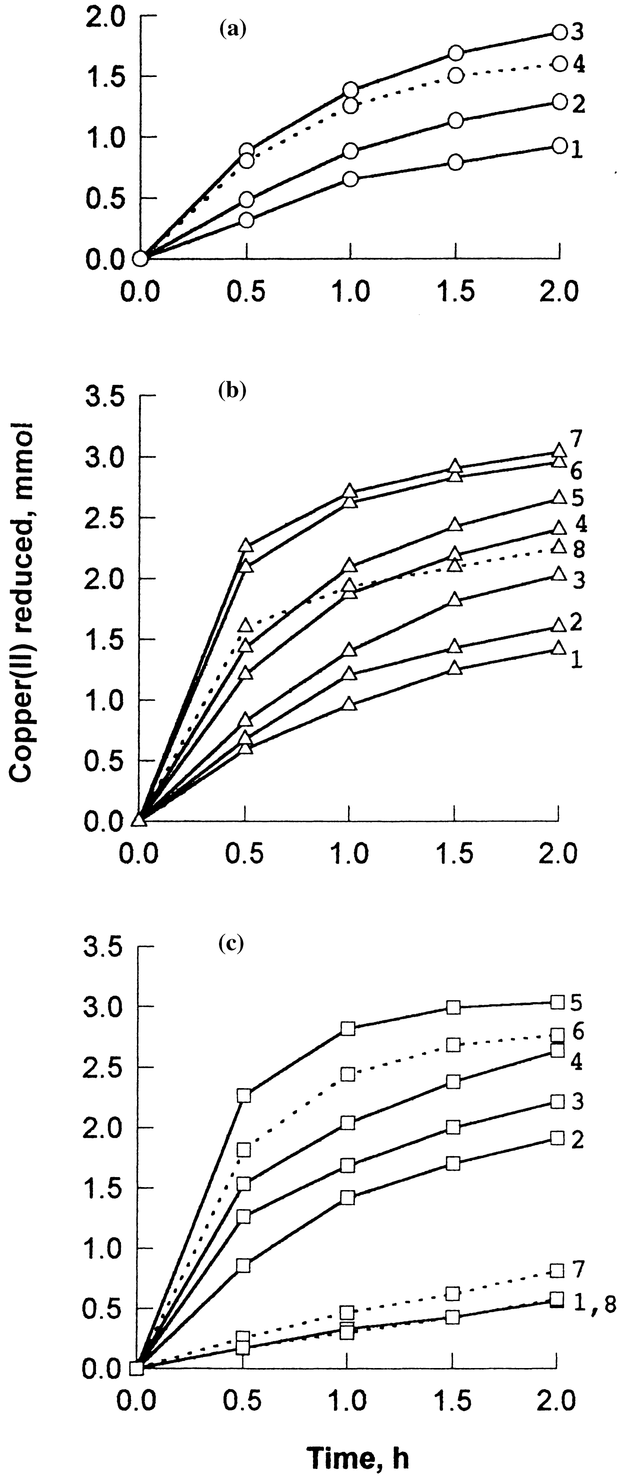

Fig. 7. Time dependence of the total amount of the Cu(II) reduced at 70 °C. Solution composition (M): $\mathrm{CuCl_2}$ 0.05, $\mathrm{CoCl_2}$ 0.15; *En*: (a) 0.4, (b) 0.6, (c) 1.2. pH (a): (1) 6.17, (2) 6.33, (3) 6.47, (4) 6.87; (b): (1) 5.72, (2) 5.81, (3) 5.93, (4) 6.13, (5) 6.57, (6) 6.89, (7) 7.72, (8) 9.71; (c): (1) 5.37, (2) 5.58, (3) 5.68, (4) 5.79, (5) 5.94, (6) 7.28, (7) 8.86, (8) 9.07.

comparing these data: (i) at 70 °C the electroless copper plating solutions are less stable in the pH region of the maximum rate of copper deposition on the surface to be plated; and (ii) the solution stability in the pH region of the largest amount of copper(II) reduced is higher in 0.6 and 1.2 M *En* solutions at 70 °C as compared with that at 50 °C, and higher rates of copper deposition on the catalytic surface are obtained in this pH region at 70 °C. An increase of solution stability at higher temperature is unusual for simple (containing no stabilizing additives) electroless plating solutions and was also observed in the case of electroless silver plating solutions using Co(II)–ammonia complex compounds [21, 22]. The effect of some 'internal' stabilizing agent (e.g., cobalt(III) compounds) could explain the atypical behaviour of the electroless plating solutions containing cobalt(II) reducing agent.

Time dependencies of the total amount of copper formed at 70 °C show a considerable influence of pH and *En* concentration on the kinetics of copper deposition (Figure 7). The main regularities are similar to those observed at 50 °C (cf. Figures 3 and 7).

Finally, it must be noted that the copper coatings obtained in the process of Cu(II) reduction by Co(II)–*En* complexes have more regular structure with lower defect level as compared with the coatings deposited at a similar rate in formaldehyde-containing solutions [23].

4. Conclusions

(i) The process of copper(II) reduction by Co(II)–ethylenediamine complex compounds depends on pH, ethylenediamine concentration and temperature.

(ii) The copper deposition process with an average rate up to 6 μm $\mathrm{h^{-1}}$ at satisfactory solution stability occurs at pH ~6 (50–70 °C).

(iii) The stoichiometry of the Cu(II) reduction reaction can be expressed by the equations:

$$\mathrm{Cu}En_2^{2+} + 2\,\mathrm{Co}En_2^{2+} \xrightarrow{\mathrm{Cu}} \mathrm{Cu} + 2\,\mathrm{Co}En_3^{3+} \quad (\mathrm{pH}\ 6\text{–}7, 50°\mathrm{C})$$

$$\mathrm{Cu}En_2^{2+} + 2\,\mathrm{Co}En_3^{2+} \xrightarrow{\mathrm{Cu}} \mathrm{Cu} + 2\,\mathrm{Co}En_3^{3+} + 2\,En \quad (\mathrm{pH} > 7)$$

(iv) A correlation exists between the rate of the copper deposition on the catalytic surface and the concentration of the $\mathrm{Co}En_2^{2+}$ complex species in the solution.

(v) The autocatalytic Cu deposition in relatively stable plating solutions occurs at low overpotentials (from −5 to −30 mV) from Cu(II)–Cu equilibrium potential.

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