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Kinetics of electroless silver deposition using cobalt(II)-ammonia complex compounds as reducing agents

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Abstract

The kinetics of electroless silver deposition from solutions containing Co(II)-ammonia complex compounds as reducing agents was studied at 20 and 50 °C. The process rate depends on the solution pH and the concentration of Ag(I), Co(II) and ammonia species. Under optimum operating conditions selected a silver deposition rate up to 1.2 μm h^{-1} can be obtained at 20 °C with high solution stability. At elevated temperature (50 °C) the rate increases and reaches $\sim$3 μm h^{-1}. The silver coatings obtained are of high quality, compact and bright.

1. Introduction

Silver(I) ions are easily reduced to the metallic state by many reducing agents but, in most cases, a silver powder is formed and it is difficult to localize the reduction process on the surface to be plated. Unstable silver(I)-ammonia complex solutions with glucose, tartrate, formaldehyde etc., as reducing agents have been used at room temperature in plating for many years. The thickness of coatings obtained from such solutions is not great, typically less than 1 μm [1–4].

More effective electroless silver plating solutions were developed using Ag(I)-cyanide complex and amineboranes [5] or hydrazine [6] as reducing agents. At 40–50 °C the deposition rate can reach 4 μm h^{-1} and in the presence of stabilizers these solutions are sufficiently stable [2, 3, 7].

The conventional electroless silver plating solutions containing the reducing agents mentioned above have some drawbacks: (i) the plating solution can not be recycled (i.e., the reducing agent oxidizes irreversibly); (ii) in the case of Ag(I)-cyanide complex the solutions are rather complicated and their use presents environmental problems; (iii) the plating rate and solution stability are not sufficiently high.

The possibility of the use of Co(II)-ammonia complex compounds as reducing agents for electroless silver deposition was shown in recent decades [8–12]. Silver plating solutions of high stability, even in the absence of stabilizing additives, were obtained, plating rate being. 1 μm h^{-1} and more. The reducing agent, Co(II), can be regenerated: its oxidation product, Co(III) species, is reducible at the lower solution pH. The silver layers obtained in the Ag(I)–Co(II)–NH_3 system have a regular structure with comparatively low levels of defects [9] and they have high protective properties when plated on copper [10].

Thermodynamic analysis showed [12] that the potential difference of the Co(II)–Co(III) and Ag–Ag(I) couples, that is, the free energy change in the silver(I) reduction by cobalt(II), depends largely on the free ammonia concentration, which is mainly determined by the total concentration of ammonium species ($NH_3 + NH_4^+$) and the solution pH. The aim of this work was to investigate systematically the influence of all main factors, solution pH, temperature, concentrations of Ag(I), Co(II) and ammonium species, on the rate of Ag deposition in the reaction

$$\mathrm{Ag(NH_3)_2^+} + \mathrm{Co(NH_3)_n^{2+}} \xrightarrow{\mathrm{Ag}} \mathrm{Ag} + \mathrm{Co(NH_3)_6^{3+}} + (n-4)\mathrm{NH_3} \qquad (1)$$

2. Experimental details

2.1. *Solutions*

Analytical grade chemicals and distilled water were used to prepare solutions. Electroless silver plating solutions were prepared as follows: the mixture of $(NH_4)_2SO_4$ and 25% NH_3 solutions was added to $AgNO_3$ solution, and then $CoSO_4$ solution was added. The main electroless silver plating solution contained (M): $AgNO_3$ 0.04, $CoSO_4$ 0.10, ($NH_4^+ + NH_3$) 2, 4 or 7. The pH was changed by changing the concentration ratio of NH_4^+ to NH_3.

2.2. *Electroless silver deposition*

Electroless coatings were deposited onto glass plates (2.0 cm × 2.5 cm) at 20 or 50 ± 1 °C. The glass surface, degreased in acid Cr(VI) solution, was sensitized in Sn(II) solution (2 g L^{-1} $SnCl_2 \cdot 2H_2O$) for 5 min, then rinsed with distilled water and activated in $AgNO_3$ solution (10 g L^{-1}). It was then immersed in the deaerated electroless silver plating solution. The reaction vessel was closed to prevent Co(II) oxidation by atmospheric oxygen. The loading was 4 dm^2 L^{-1}.

2.3. *Analytical procedures*

The amount of silver deposited onto the glass plate was determined by weighing. The total amount of Ag reduced (on the surface plated and in the solution bulk) was determined by potentiometric titration with 0.01 M KI solution, using an Ag indicator electrode and a glass electrode as reference. The Co(II) concentration was determined titrimetrically [13].

3. Results and discussion

3.1. *Electroless silver deposition at 20 °C*

The reduction of Ag(I) ions by Co(II) in ammonia containing solutions takes place at pH over 8, and the lower pH limit of Ag deposition decreases with the increase in the total ammonium compound concentration (Figure 1). Thermodynamically silver(I) reduction by cobalt(II) can occur even at pH 6.0–6.5 [12]. The lower pH limit of silver deposition shifts with ammonium species concentration in the same direction as predicted by calculations. The practically observed lower pH limit of silver plating solutions (8.5–9.5) corresponds to a rather high value of the redox couples Co(II)–Co(III) and Ag–Ag(I) potential difference about −200 mV [12].

When comparing the lower pH limit of silver deposition with the Co(II)-ammonia complex formation equilibria in the solutions under investigation [12], it can be concluded that Ag(I) reduction by Co(II)-ammonia complexes begins when an appreciable amount of hexacoordinated complex $Co(NH_3)_6^{2+}$ (over 5% of the total Co(II) concentration) appears in the solution.

The solution pH range for electroless silver deposition depends on the ammonium species concentration: at 2 M (NH_3 + NH_4^+) this pH interval is 9.2–11, and at 7 M it rises to 8.5–12.5.

The maximum deposition rate is larger and is obtained at higher solution pH values at higher ammonia–ammonium salt concentration: at 2, 4 and 7 M (NH_3 + NH_4^+) the highest rates are observed at pH 10.2, 10.85 and 11.2, respectively. Comparison of these results with the data of Co(II) distribution among the complexes in this system [12] shows that the highest possible concentration of $Co(NH_3)_6^{2+}$ complex is reached at these conditions. Thus, $Co(NH_3)_6^{2+}$ may be assumed to be the active complex participating in the autocatalytic reduction reaction.

At higher pH, after reaching a distinct maximum, a sharp decrease in plating rate is observed (Figure 1). This phenomenon may be related to changes in the silver surface state as the result of Co(II), Co(III), and/or Ag(I) complexes hydrolysis and deposition of hydrolysis products at higher solution pH. For example, cobalt(II) hydroxide should form in the solutions under study at pH 10.8 (2 M (NH_4^+ + NH_3)), and at pH 11.8 (4 M (NH_4^+ + NH_3)), according to the complex equilibria calculations. These pH values coincide approximately with the experimental upper pH limit for silver plating. Some enhancement of hydrolysed species formation by

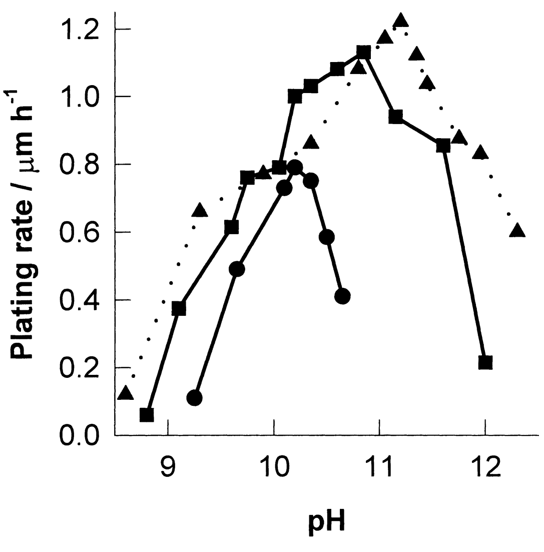

Fig. 1. Dependence of the silver deposition rate on solution pH at 20 °C. Solution contained (M): $AgNO_3$ 0.04; $CoSO_4$ 0.10; (NH_3 + NH_4^+): ● 2, ■ 4, and ▲ 7.

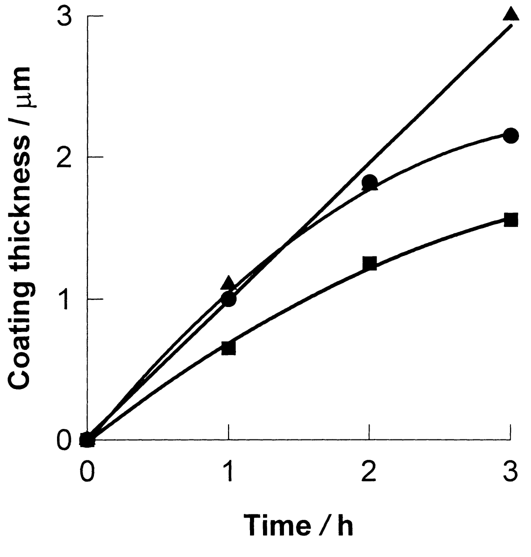

Fig. 2. Kinetics of silver deposition at 20 °C. Solution contained (M): $AgNO_3$ 0.04; $CoSO_4$ 0.10; (NH_3 + NH_4^+): ■ 2 (pH 10.15), ● 4 (pH 10.85) and ▲ 7 (pH 11.2).

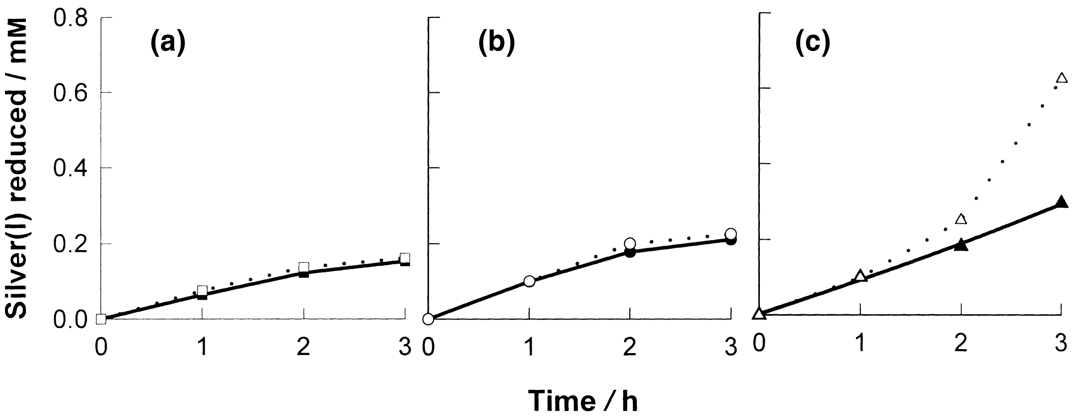

Fig. 3. Kinetics of silver deposition on the surface to be plated (black marks) and of total silver(I) reduction process (white marks) at 20 °C. Solution contained (M): $AgNO_3$ 0.04; $CoSO_4$ 0.10; (NH_3 + NH_4^+): (a) 2 (pH 10.15), (b) 4 (pH 10.85) and (c) 7 (pH 11.2).

the silver surface may be involved at lower pH, in homogeneously stable solutions; Ag_2O deposition on silver was shown to occur in Ag(I)-ammonia solutions [14].

The possible effect of changing the redox potential difference of Co(II)–Co(III) and Ag–Ag(I) couples [12] – at higher solution pH this difference becomes less negative – is not so important as the hydrolysis effects.

Longer silver plating experiments at the conditions of the highest silver deposition rate showed that coatings with thickness up to 3 μm could be obtained from the solutions investigated without additional replenishment of the reactants for 3 h (Figure 2).

The amount of Ag deposited and Ag(I) concentration changes in the solution bulk showed (Figure 3) that the proportion of Ag(I) reduced in the solution bulk is small as compared with the total amount of Ag(I) reduced in 2 and 4 M ammonia–ammonium salt containing solutions. At higher ammonia–ammonium salt concentrations (7 M) the instability of the solutions is higher, after 3 h the amount of silver deposited on the surface is approximately equal to that reduced in the solution bulk (Figure 3(c)).

At constant Co(II) concentration, the coating thickness depends very strongly on Ag(I) concentration in the range 0.01–0.04 M (Figure 4). In 4 M ammonia–ammonium salt solution, the rate maximum is not distinct and the highest rate (~1.2 μm h^{-1}) is observed at 0.07 M Ag(I) (Figure 4, curve 1). A similar highest plating rate was observed in 7 M ammonia–ammonium salt solution, but the concentration dependence had a distinct maximum at 0.04 M silver(I) (Figure 4, curve 2).

It should be noted that the stability of the plating solution containing 7 M ammonia–ammonium salt is high enough at the highest plating rate conditions. In the case of 4 M ammonia–ammonium salt concentration the solutions are considerably less stable in the Ag(I) concentration region where the highest plating rates are observed. The sufficiently high stability is observed only at relatively low (0.05 M) or relatively high (0.09 M) Ag(I) concentrations.

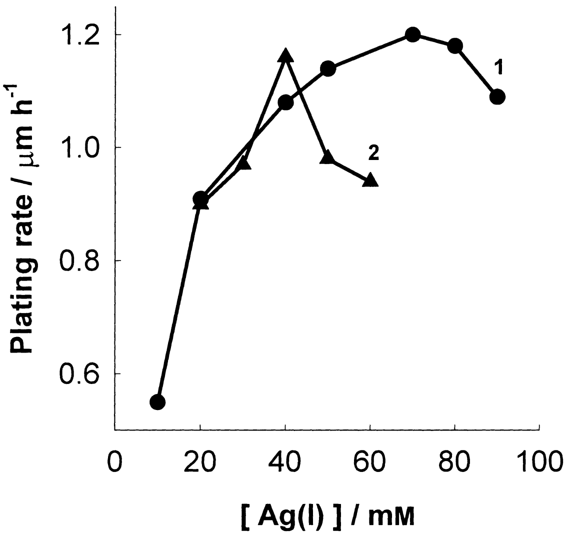

Fig. 4. Dependence of thickness of silver coating deposited in 1 h at 20 °C on Ag(I) concentration. Solution contained (M): $CoSO_4$ 0.10; (NH_3 + NH_4^+): ● 4 (pH 10.85), ▲ 7 (pH 11.2).

At constant silver(I) concentration in 7 M ammonia–ammonium salt solution the thickness of the silver deposits depends linearly on Co(II) concentration in the range 0.05 to 0.3 M (Figure 5). In 4 M ammonia–ammonium salt solution the amount of silver reduced increases to 0.2 M of Co(II), and further increase in Co(II) concentration does not influence the silver reduction rate. This constancy of plating rate at Co(II) concentration over 0.2 M can be explained by the solution equilibria: the concentration of the active $Co(NH_3)_6^{2+}$ complex does not rise with increase in total Co(II) concentration due to the relatively low excess of ammonia compounds.

In terms of plating rate–solution pH dependence at different Co(II) concentrations, the plating rate maximum values shift to lower pH with increase in Co(II) concentration (Figure 6). Taking into account the decrease in free ammonia and ammonium ion concentration with increasing total Co(II) concentration this shift

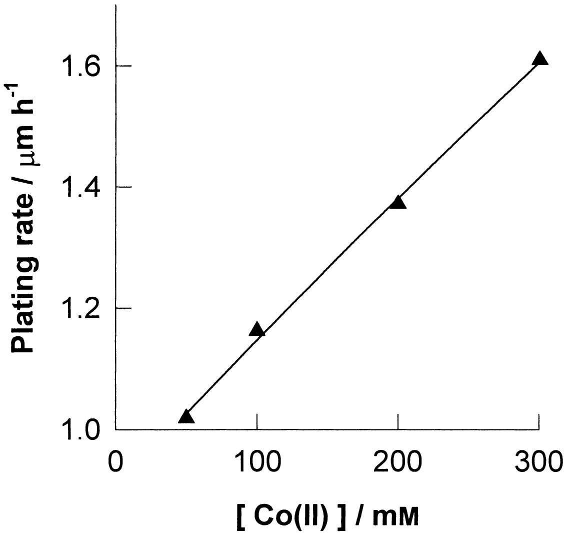

Fig. 5. Dependence of thickness of silver coating deposited in 1 h at 20 °C on Co(II) concentration. Solution contained (M): AgNO$_3$ 0.04; (NH$_3$ + NH$_4^+$) 7 (pH 11.2).

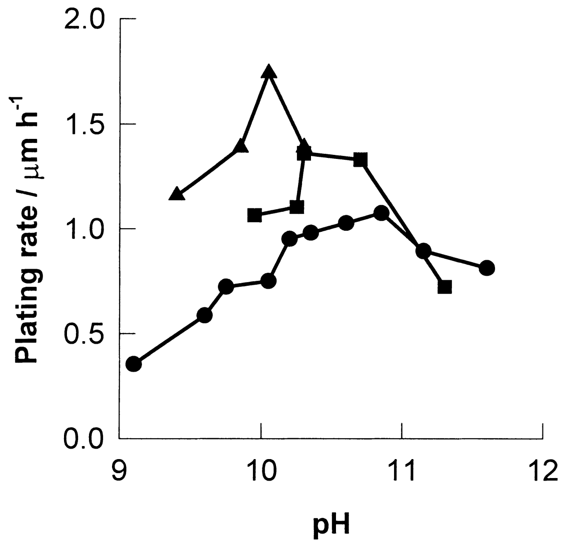

Fig. 6. Dependence of thickness of silver coating deposited in 1 h at 20 °C on solution pH. Solution contained (M): AgNO$_3$ 0.04; (NH$_3$ + NH$_4^+$) 4; CoSO$_4$: ● 0.10, ■ 0.20, and ▲ 0.40.

may to some extent be attributed to changes in the Co(II)-ammonia complex distribution (Figure 1).

Solution stability diminishes with increase in total Co(II) concentration at the conditions of highest plating rate, and in practice a concentration of 0.1 M Co(II) should be not exceeded. Thus, the 0.04 M Ag(I) and 0.1 M Co(II) concentrations can be considered as close to optimal under the studied conditions.

It is known that Co(II) can be oxidized by atmospheric oxygen in aqueous alkaline amine solutions forming dioxygen complexes [15–17]. Therefore, it is important to understand the behaviour of the solutions under investigation with access of oxygen. Additional experiments carried out under conditions corresponding to the highest silver deposition rate showed that the amount of Co(II) oxidized decreased with increase in the ammonia–ammonium salt concentration and pH (Figure 7). When comparing the results with those from the similar Co(II)–ethylenediamine system, where the rate of Co(II) oxidation by atmospheric oxygen increases with increase in solution pH [18], it can be seen that the Co(II)-ammonia system behaves in a reverse manner.

The different behaviour of these two systems can be related to the different activity of Co(II) complex species in the reaction with oxygen. In the Co(II)–ethylenediamine system the active species are tetra- and hexacoordinated complexes CoEn_2^{2+} and CoEn_3^{2+}, and with increase in pH (e.g., from 5 to 7) the concentration of these species, as well as the oxidation rate increases [18]. In the Co(II)–ammonia system, in contrast, the tetracoordinated complex Co(NH$_3$)$_4^{2+}$ is inactive in the oxidation reaction, and the active species are penta- and hexacoordinated Co(II) complexes Co(NH$_3$)$_5^{2+}$ and Co(NH$_3$)$_6^{2+}$, the reactivity of Co(NH$_3$)$_6^{2+}$ being lower as compared with Co(NH$_3$)$_5^{2+}$ [19, 20].

The data of Figure 7 can be correlated with the equilibrium concentration of Co(NH$_3$)$_5^{2+}$ in the solutions under investigation. Calculations performed on the basis of [12] showed that this concentration decreased with increase in ammonia–ammonium salt concentration and pH from 55% to 48% and 37% of total Co(II).

3.2. *Electroless silver deposition at 50 °C*

In this case the autocatalytic reduction of Ag(I) ions by Co(II) complexes with ammonia occurs at pH > 7 (Figure 8). The plating rate increases almost linearly with increase in pH up to pH ~9 and 10 for solutions with different ammonium species concentration (Figure 8). These data correlate with the free energy

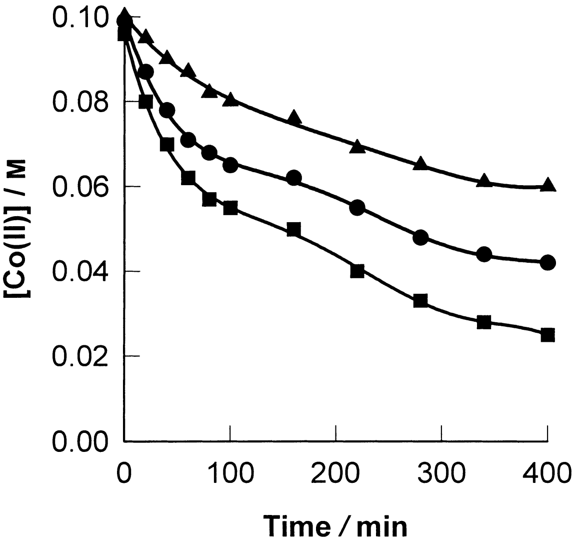

Fig. 7. Kinetics of Co(II) oxidation by atmospheric oxygen under the natural aeration conditions at 20 °C. Solution contained (M): CoSO$_4$ 0.10; (NH$_3$ + NH$_4^+$): ■ 2 (pH 10.15), ● 4 (pH 10.85) and ▲ 7 (pH 11.2).

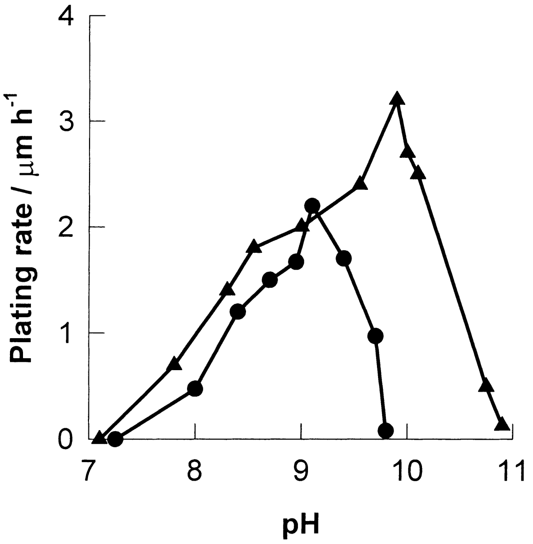

Fig. 8. Dependence of the silver deposition rate on solution pH at 50 °C. Solution contained (M): $AgNO_3$ 0.04; $CoSO_4$ 0.10; (NH_3 + NH_4^+): ● 4 and ▲ 7.

change for Ag(I) reduction by Co(II) in the solutions studied [12].

The dependence of coating thickness on solution pH shows a distinct maximum. The maximum shifts to higher pH with increase in total ammonia–ammonium ion concentration. The thickness of the coatings obtained at the optimum operating conditions reaches 2.2 µm h^{-1} (pH 9.1; 4 M (NH_4^+ + NH_3)) and 3.2 µm h^{-1} (pH 9.9; 7 M (NH_4^+ + NH_3)) respectively (Figure 8). The solutions investigated were stable, no considerable signs of silver(I) reduction in the solution bulk were observed.

The rather sharp decrease in silver deposition rate at higher pH is, apparently, connected with the same changes in the cobalt or silver complexes (hydrolysis) as discussed for 20 °C.

The determination of Ag(I) concentration in the solution and the calculation of the total amount of silver reduced confirmed the visual observations; the part of Ag(I) reduced in the solution bulk is rather low and, at the highest rates, does not exceed 10%. The solution stability is higher at higher concentrations of ammonia compounds. The Ag(I) concentration changes also show that the decrease in Ag deposition rate at higher pH is not connected with solution instability.

Longer time plating experiments showed that silver coatings with thickness greater than 7 µm could be obtained without replenishment of the solution over 3 h

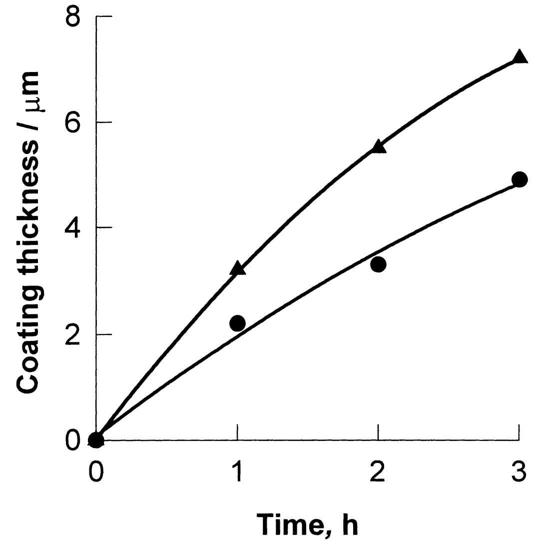

Fig. 9. Kinetics of silver deposition at 50 °C. Solution contained (M): $AgNO_3$ 0.04; $CoSO_4$ 0.10; (NH_3 + NH_4^+): ● 4 (pH 9.1) and ▲ 7 (pH 9.9).

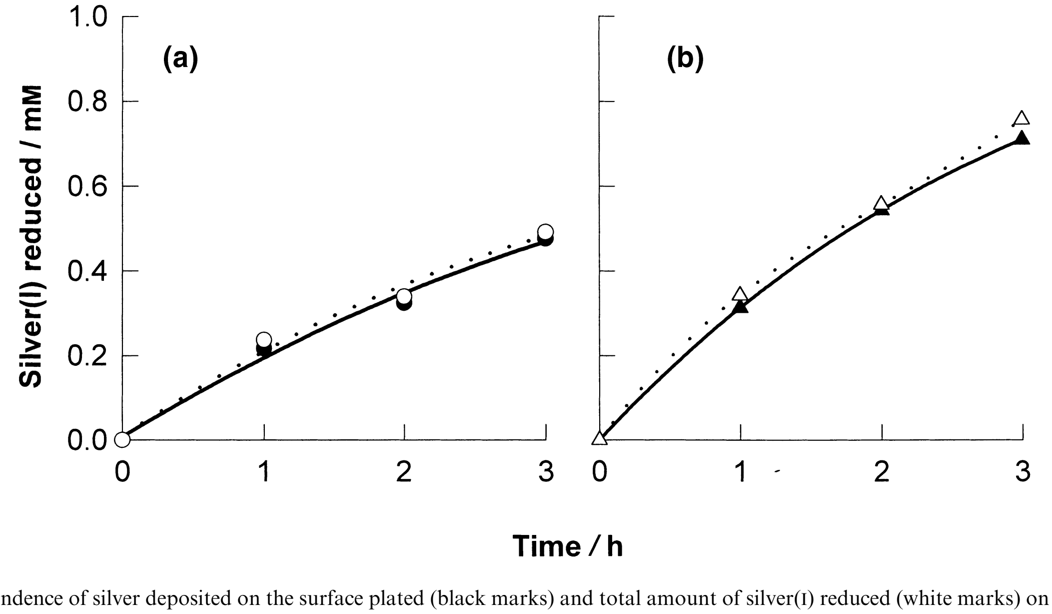

Fig. 10. Dependence of silver deposited on the surface plated (black marks) and total amount of silver(I) reduced (white marks) on time at 50 °C. Solution contained (M): $AgNO_3$ 0.04; $CoSO_4$ 0.10; (NH_3 + NH_4^+): (a) 4 (pH 9.1) and (b) 7 (pH 9.9).

(Figure 9). The solutions were stable during the process and the reduction of silver(I) occurred only on the surface plated (Figure 10). This behaviour is atypical for electroless plating solutions containing no stabilizing additives, usually at higher plating rates metal ion reduction in bulk solution occurs immediately or after 1–2 h.

When comparing the results with those for 20 °C, it is seen that the rate of silver deposition and the solution stability increases with increase in temperature. The highest deposition rate at 50 °C is more than twice higher than that at 20 °C. The solution pH region of silver deposition shifts to lower pH (at 20 °C the region is 9–12, at 50 °C it is from 7 to 10 or 11). The larger part of this pH shift is due to the difference in the pH scales at 20 °C and 50 °C (pH of the same solution is lower by 1.0–1.5 pH units at 50 °C as compared to that at 20 °C). But some pH shift occurs, apparently, as the result of kinetic enhancement of the Ag(I) reduction and surface passivation. Higher solution stability at higher temperature is an unusual and unexpected phenomenon in solutions containing no stabilizers. Apparently, the system itself contains species producing a stabilizing effect (e.g., a cobalt(III) compound).

The silver coatings obtained at elevated, as well as at room, temperature are of high quality, compact and bright, similar to the silver deposits electroplated from cyanide bath. They have a regular structure with low levels of defects [9]. The results suggest that electroless silver plating using Co(II) as a reducing agent is more effective at elevated temperatures.

4. Conclusions

(i) Silver(I) reduction by means of cobalt(II)–ammonia complex compounds depends on the solution pH, Ag(I), Co(II) and ammonium species concentration.
(ii) Autocatalytic silver deposition occurs when an appreciable amount of hexacoordinated complex $Co(NH_3)_6^{2+}$ is present in the solution.
(iii) The silver plating rate at the optimum operating conditions is about 1.2 μm h^{-1} at pH 11.2 (20 °C), and 3.2 μm h^{-1} at pH 9–10 (50 °C).
(iv) Compact and bright silver coatings of high quality up to 7 μm thick can be obtained in 3 h at 50 °C.
(v) The silver plating solutions are of high stability without the addition of stabilizing agents.
(vi) In the region of the highest silver deposition rates the Co(II) oxidation rate by atmospheric oxygen decreases with increase in ammonium species concentration.

References

1. A. Vaškelis, *in* D. Satas (Ed.), 'Coatings Technology Handbook' (Marcel Dekker, New York, 1991), p. 187.
2. A. Vaškelis and M. Šalkauskas, *in* D. Satas (Ed.), 'Plastics Finishing and Decorations' (Van Nostrand Reinhold Co., New York, 1986), p. 287.
3. G.O. Mallory and J.B. Hajdu (Eds), '*Electroless Plating: Fundamentals and Applications*' (American Electroplaters and Surface Finishers Society, Orlando, 1990), p. 539.
4. M. Šalkauskas and A. Vaškelis, '*Chemical Metallizing of Plastics*' (Khymia, Leningrad, 1985), p. 144 (in Russian).
5. F. Pearlstein and R.F. Weightman, *Plating* **58** (1971) 1014; *ibid.* **61** (1974) 154.
6. A. Vaškelis and O. Diemontaitė, *Trans. Lithuanian Acad. Sci. B* **4(89)** (1975) 23; *B* **5(96)** (1976) 3.
7. N. Koura and A. Kubota, *J. Met. Finish. Soc. Jpn.* **36** (1985) 182.
8. A. Vaškelis and O. Diemontaitė, *Trans. Lithuanian Acad. Sci. B* **1(116)** (1980) 3.
9. A. Vaškelis, A. Jagminienė, R. Juškėnas, E. Matulionis and E. Norkus, *Surf. Coat. Technol.* **82** (1996) 165.
10. A. Vaškelis and A. Jagminienė, *Zashchita Metallov (Moscow)* **25** (1989) 305.
11. A. Vaškelis, E. Norkus, G. Rozovskis and J. Vinkevičius, *Trans. Inst. Metal Finish.* **75** (1997) 1.
12. A. Vaškelis and E. Norkus, *Electrochim. Acta* **44** (1999) 3667.
13. E. Norkus, *Talanta* **47** (1998) 1297.
14. A. Vaškelis and O. Diemontaitė, *Trans. Lithuanian Acad. Sci. B* **5** (1978) 13.
15. R.D. Jones, D.A. Summerville and F. Basolo, *Chem. Revs.* **79** (1979) 139.
16. E.C. Niederhoffer, J.H. Timmons and A.E. Martell, *Chem. Revs.* **84** (1984) 137.
17. D.M. Palade, *Koord. Khim.* **18** (1992) 729.
18. E. Norkus, A. Vaškelis, A. Grigucevičienė, G. Rozovskis, J. Reklaitis and P. Norkus, *Transition Metal Chem.* **26** (2001) 465–472.
19. M. Mori, J.A. Weil and M. Ishiguro, *J. Am. Chem. Soc.* **90** (1968) 615.
20. J. Simplicio and R.G. Wilkins, *J. Am. Chem. Soc.* **91** (1969) 1325.