CHEMIJA. 2007. Vol. 18. No. 1. P. 8–13

Thermodynamical aspects of copper(II) reduction process by cobalt(II)–diethylenetriamine complexes

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Calculations show that cobalt(II) complexes with diethylenetriamine (*dien*) are rather strong reducing agents and are capable of reducing copper(II) ions to the metallic state and therefore can be used in electroless plating systems for the deposition of copper coatings. A thermodinamic analysis of equilibria in a system Cu–Cu(II)–Co(II)–Co(III)–diethylenetriamine (*dien*) was carried out and the conditions of Cu(II) reduction to metal by Co(II) were predicted. Copper(II) reduction is supposed to occur in pH region from ca. 5 to ca. 9.5 (20 °C). The reduction process is predicted to be strongly dependent on the solution pH and ligand (*dien*) concentration. The most negative difference of a redox potential (DE) between Cu(II)/Cu and Co(III)/Co(II) couples could reach value of –200 mV. The highest metal deposition rate in the absence of considerable metal formation in the solution bulk was obtained in solutions with predominating Co(II) complexes Co*dien*$^{2+}$ and Co*dien*$_2^{2+}$ at the above-mentioned pH values.

Key words: electroless copper plating, cobalt(II)–diethylenetriamine complexes, copper(II) reduction

INTRODUCTION

Cobalt(II) complex with ethylenediamine was found [1] to be an effective reducing agent in the autocatalytic reduction of copper(II) to metal (electroless copper plating). A thermodynamical analysis and kinetical investigations were carried out for copper deposition in this system [2–6], and rather high rate of reduction on the metal surface without any appreciable bulk reduction was observed at certain reactant concentrations and solution pH. This electroless copper deposition method may be of practical importance due to several specific features: a less-defective structure of the copper layers because of the absence of hydrogen evolution and its inclusion into the deposits, a possibility to regenerate the reducing agent (cobalt(III) is reducible to the initial cobalt(II) complex electrochemically or chemically, in contrast to the conventional reducing agents).

Co(II) complexes with other diamines, such as propane-1,2-diamine (propylenediamine) were also shown to be sufficiently strong to reduce copper(II) to the metallic state and suitable to be used as reducing agents in electroless copper plating solutions [7].

In recent comparative studies of various amines in alkaline Co(II) solutions [8–10], diethylenetriamine (*dien*) $H_2N–CH_2–CH_2–NH–CH_2–CH_2–NH_2$ was shown to enhance the anodic oxidation of cobalt(II) effectively. This effect was explained by the formation of easily oxidizable and active Co(II) complexes with *dien*. The anodic oxidation of a reducing agent is one of the two partial electrochemical reactions in the autocatalytic (electroless) metal deposition process, and its rate is usually the main factor determining the overall electroless process rate. Therefore, the anodic oxidation data on cobalt(II)–*dien* complexes were used in constructing new electroless metal plating solutions.

As it has been described earlier [9, 10], the reducing activity of Co(II)–*dien* complexes is similar or even higher than that of ethylenediamine complexes. They are able to reduce copper(II) ions to metal autocatalytically. This Cu(II) reduction process by Co(II)–amine complexes was shown to be very sensitive to the solution pH and anions present in the solution [11–13]. In most cases, the autocatalytic copper(II) reduction by cobalt(II)–*dien* complex occur at the solution pH over 4. The copper deposition rate reaches its maximum at pH 5–7, falls down at higher solution pH values and at pH 9–10 copper deposit formation practically stops. The decrease of copper deposition rate was explained by the enhancement of copper(II) reduction in the whole solution volume (solution instability) at higher solution pH because of thermodynamical reasons – a higher degree of cobalt(II) complexation and a shift of the Co(III)/Co(II) couple redox potential to more negative values.

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Previously published data indicate that the cobalt(II)–*dien* complex is the most active reducing agent among all cobalt(II)–amine complexes used for electroless copper deposition [11].

This work is aimed at a thermodynamic analysis of Cu–Cu(II)–Co(II)–Co(III)–diethylenetriamine(*dien*) system, since no data on this issue are documented in literature.

Additionally, a practical process of copper(II) reduction by cobalt(II) in *dien* solutions was studied by the electrochemical quartz crystal microgravimetry (EQCM). This method allows instantaneous copper deposition rate measurements.

EXPERIMENTAL

The distribution of Co(II), Co(III), Cu(II) among the complexes with diethylenetriamine was calculated by solving the system of non-linear equations in terms of the Newton iteration method [14], using metal-ion complex stability and ligand protonization constants. The possibility of Co(II) and Co(III) hydroxide formation was considered as well. The following values of the standard redox potentials were used:

$$E^0_{Co^{3+}/Co^{2+}} = 1.82 \text{ V and}$$

$$E^0_{Cu^{2+}/Cu} = 0.345 \text{ V.}$$

Analytical grade chemicals and triply distilled water were used to prepare the solutions. The solutions contained (mol l^{-1}): Cu(II) chloride – 0.05, Co(II) chloride – 0.15, diethylenetriamine (*dien*) – 0.6. The pH value of the solutions was adjusted by using hydrochloric acid. Electroless plating solutions were prepared as follows: necessary amounts of water, Cu(II) salt solution, acid and Co(II) salt solution were mixed in a reaction vessel, oxygen was removed from the solution by bubbling Ar, and *dien* was added. Electroless plating was carried out in a closed glass vessel enabling to work at an inert atmosphere by passing Ar through the solution or over it.

Prior to the measurements, a layer of copper was electrodeposited on a gold sublayer onto quartz crystals installed at the bottom of the cell from a solution containing 1.0 mol l^{-1} $CuSO_4$ and 0.5 mol l^{-1} H_2SO_4 at a current 10 mA for 1 min.

The details of the employed EQCM set-up have been described elsewhere [11, 15, 16]. AT-cut quartz crystals of fundamental frequency of 6 MHz (from Intelemetrics Ltd., UK) sputtered by gold from both sides were used. Their electrochemically and piezoelectrically active geometric areas were 0.636 and 0.283 cm^2, respectively.

The quartz crystals were installed at the bottom of the cell with a working volume of *ca.* 2 ml. The upper part of the cell contained a Pt-wire, the joints for the electrolyte inlet and the Luggin capillaries, and the electrolyte outlet tube. EQCM measurements were carried out in unstirred solutions (under stopped-flow conditions).

The potential has been measured with respect to Ag/AgCl/KCl$_{sat}$ reference electrode and is given below versus the standard hydrogen electrode (SHE). In the case of Cu deposition, a theoretical calibration constant, –41 Hz s^{-1} mA^{-1}, calculated from the Sauerbray's equation for 6 MHz quartz crystal [17] was used for converting the counted frequency to the current units. This corresponds to the sensivity of the EQCM used 0.08 Hz ng^{-1} cm^2.

All experiments were carried out at 20 ± 1 °C.

RESULTS AND DISCUSSION

In this work a thermodynamic analysis of equilibria in systems Cu–Cu(II)–Co(II)–Co(III)–diethylenetriamine was carried out and the conditions of Cu(II) reduction to metal by Co(II) were predicted.

Initially the distribution of the *dien* forms in a wide pH range was calculated using ligand protonation constants given in [18, 19]:

$$\mathit{dien} + H^+ \underset{\longleftarrow}{\xrightarrow{K_{a1}}} \mathit{dien}H^+ \quad 20\ °C \quad \log K_{a1} = 9.94 \qquad (1)$$

$$\mathit{dien}H^+ + H^+ \underset{\longleftarrow}{\xrightarrow{K_{a2}}} \mathit{dien}H_2^{2+} \quad 20\ °C \quad \log K_{a2} = 9.13 \qquad (2)$$

$$\mathit{dien}H_2^{2+} + H^+ \underset{\longleftarrow}{\xrightarrow{K_{a3}}} \mathit{dien}H_3^{3+} \quad 20\ °C \quad \log K_{a3} = 4.34 \qquad (3)$$

Diethylenetriamine molecules were protonated in an acidic medium and the triply protonated form of $\mathit{dien}H_3^{3+}$ was the predominant form of *dien* when pH was lower than 4. While pH of the solution was increasing, one proton splited of from $\mathit{dien}H_3^{3+}$, and when pH was about 6, the diprotonated form of $\mathit{dien}H_2^{2+}$ predominated. After the pH value of the solution reached 9.5, the monoprotonated form of $\mathit{dien}H^+$ prevailed. The further

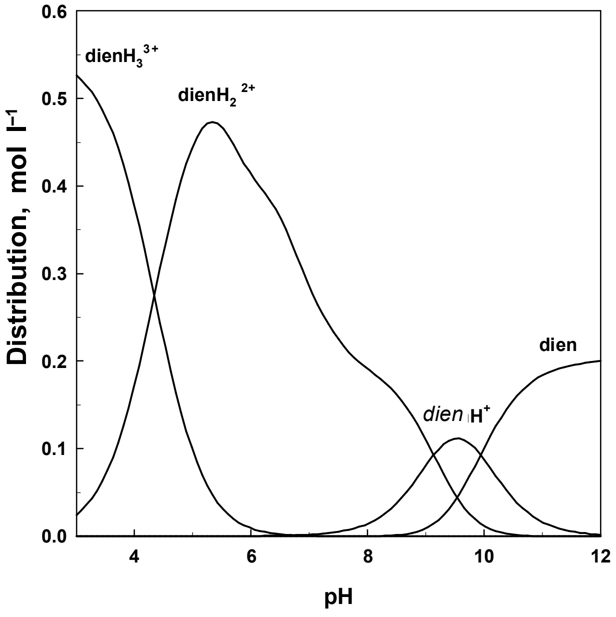

Fig. 1. Distribution of *dien* forms in solutions containing (mol l^{-1}): *dien* – 0.6, Cu(II) – 0.05, Co(II) – 0.15. 20 °C

increase of the pH led to the full deprotonation of the *dien* (Fig. 1).

In the next step, the distribution of Co(III), Co(II) and Cu(II) among the complexes with *dien* was calculated using metal-ion stability constants as well as ligand protonation constants given in [18–20].

Co(III) composes very stable complexes with amines. Co(III) complex with *dien* can be characterized by the following equilibrium constant of di-ligand complex formation [20]:

$$\mathrm{Co}^{3+} + 2dien \underset{\longleftarrow}{\overset{\beta_2}{\longrightarrow}} \mathrm{Co}dien_2^{3+} \quad 20\ ^\circ\mathrm{C} \quad \log b_2 = 48 \qquad (4)$$

Due to the high stability of the complex, it predominates over the whole range of the solution pH studied by us. Hence, in our system Co(III) is always in the form of Co*dien*$_2^{3+}$ ions.

Co(II) forms two complexes with *dien*: Co*dien*$^{2+}$ and Co*dien*$_2^{2+}$. The stability of the complexes is characterized by the following equilibrium constants:

$$\mathrm{Co}^{2+} + dien \underset{\longleftarrow}{\overset{\beta_1}{\longrightarrow}} \mathrm{Co}dien^{2+} \quad 20\ ^\circ\mathrm{C} \quad \log\beta_1 = 8.10 \qquad (5)$$

$$\mathrm{Co}^{2+} + 2dien \underset{\longleftarrow}{\overset{\beta_2}{\longrightarrow}} \mathrm{Co}dien_2^{2+} \quad 20\ ^\circ\mathrm{C} \quad \log\beta_2 = 14.10 \qquad (6)$$

In an acidic medium when pH is lower than 4.5, Co(II) does not form any complexes with *dien*. While increasing pH of the solution the concentration of the uncomplexed Co(II) ions decreases, since Co*dien*$^{2+}$complex is formed. This complex becomes predominant when pH is about 6. Further increasing the solution pH, the concentration of Co*dien*$^{2+}$ decreases, while the concentration of a newly appeared complex of Co*dien*$_2^{2+}$ begins to increase. At pH values higher than 8, Co(II) exists in the solution in the form of Co*dien*$_2^{2+}$ (Fig. 2).

The distribution of the complexes is related to the deprotonation of diethylenetriamine in more alkaline solutions.

Cu(II) also forms two complexes with *dien*, namely Cu*dien*$^{2+}$ and Cu*dien*$_2^{2+}$, and a mixed hydroxycomplex of Cu*dien*(OH)$^+$ at higher pH values. The stability constants of these complexes according to [18, 19] are listed below:

$$\mathrm{Cu}^{2+} + dien \underset{\longleftarrow}{\overset{\beta_1}{\longrightarrow}} \mathrm{Cu}dien^{2+} \quad 20\ ^\circ\mathrm{C} \quad \log\beta_1 = 16.7 \qquad (7)$$

$$\mathrm{Cu}^{2+} + 2dien \underset{\longleftarrow}{\overset{\beta_2}{\longrightarrow}} \mathrm{Cu}dien_2^{2+} \quad 20\ ^\circ\mathrm{C} \quad \log\beta_2 = 21.5 \qquad (8)$$

$$\mathrm{Cu}dien^{2+} + \mathrm{OH}^- \rightarrow \mathrm{Cu}dien(\mathrm{OH})^+ \quad 20\ ^\circ\mathrm{C} \quad \log K = 4.75 \qquad (9)$$

$$\mathrm{Cu}^{2+} + dien + \mathrm{OH}^- \underset{\longleftarrow}{\overset{\beta_2}{\longrightarrow}} \mathrm{Cu}dien(\mathrm{OH})^+ \quad 20\ ^\circ\mathrm{C}$$

$$\log\beta_{11} = 21.45 \qquad (10)$$

In an acidic medium, when pH is higher than 3.5, practically all Cu(II) exists in the form of Cu*dien*$^{2+}$. The Cu*dien*$_2^{2+}$ complex appears in the solution at pH over 6 and predominates at pH values over 8.5. In contrast to the Co(II)–*dien* system, an additional mixed hydroxycomplex, Cu*dien*(OH)$^+$, appears at pH higher than 12 (Fig. 3).

The concentrations of free (uncomplexed) Co^{2+} and Cu^{2+} ions were calculated using the data on the distribution of these metal ions among the complexes with *dien* in the wide range of solution pH (3–12). The obtained results are shown in Fig. 4. It can be stated that Cu^{2+} ions form stronger complexes than Co^{2+} ions, as pCu reaches 22 and pCo reaches only just 13. The concentration of Cu^{2+} ions starts to decreasing at rather low solution pH (lower than 3), and the concentration of Co^{2+} ions decreases only from

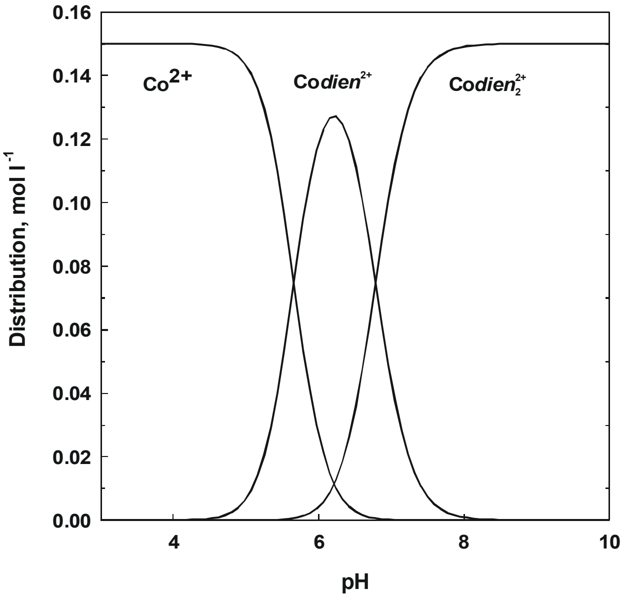

Fig. 2. Distribution of Co(II) among the complexes with *dien* in solutions containing (mol l^{-1}): *dien* – 0.6, Cu(II) – 0.05, Co(II) – 0.15. 20 °C

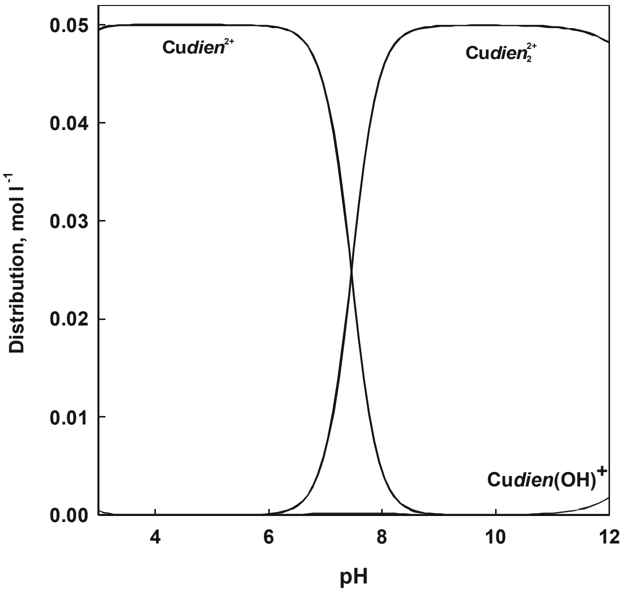

Fig. 3. Distribution of Cu(II) among the complexes with *dien* in solutions containing: (mol l^{-1}): *dien* – 0.6, Cu(II) – 0.05, Co(II) – 0.15. 20 °C

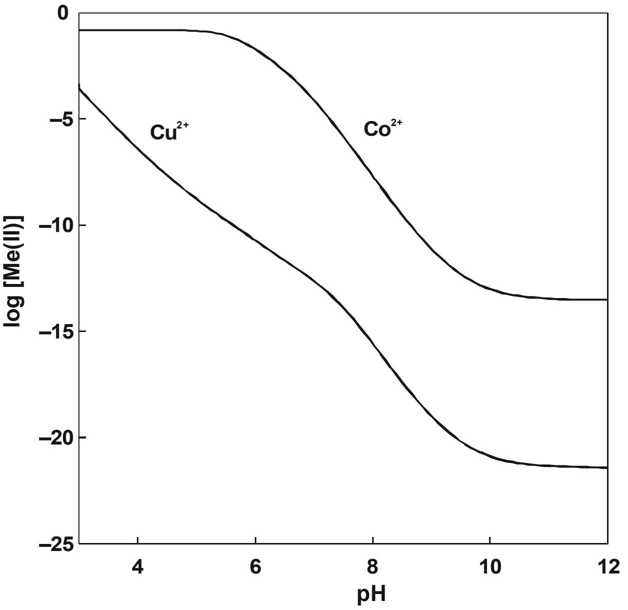

Fig. 4. Relationship of log[Me(II)] to pH in solutions containing (mol l^{-1}): *dien* – 0.6, Cu(II) – 0.05, Co(II) – 0.15. 20 °C

pH 6. However, the ions of both metals are strongly chelated when the solution pH reaches 10 (Fig. 4).

The redox potentials of the systems Co(III)/Co(II) and Cu(II)/Cu were calculated using Nernst's equation by using the calculated values of the concentrations of free Cu(II), Co(II), Co(III) ions and the standard potentials of both systems given above.

The potential of the cobalt(III)/cobalt(II) redox couple was calculated for the case, when the solution contained 1% of Co(III) and 99% of Co(II) ions. This situation can be observed at the initial point of the electroless metal deposition when the compounds of Co(III) are not added to the solution, but they are formed when Co(II) is oxidized.

The redox potential of the system Co(III)/Co(II) in the *dien* solution highly depends on the solution pH. While increasing the pH value from 3 to 6, the redox potential of this system becomes more negative and reaches the constant value of ca. –0,2 V, when the solution pH is 7 (Fig. 5a, curve 1). In the case of the copper/copper(II) system, a clear dependence of the shift of Cu equilibrium potential to more negative values on the solution pH is observed in the pH range 3–9.5 (Fig. 5a, curve 2). The Co(III)/Co(II) potential becomes more negative than that of Cu(II)/Cu in the pH range from 5 to 9.5. Furthermore, when the solution pH value exceeds 9.5, the potential of Cu(II)/Cu system again becomes more negative in comparison to the Co(III)/Co(II) system (Fig. 5 a).

The difference between the potentials of Co(III)/Co(II) and Cu(II)/Cu redox couples at 20 °C can be expressed as follows:

$$\Delta E = (E^0_{\mathrm{Co(III)/Co(II)}} - E^0_{\mathrm{Cu(II)/Cu}}) + \\ + 0.029 \log\left(\frac{[Co^{3+}]^2}{[Co^{2+}]^2[Cu^{2+}]}\right) \tag{11}$$

For the calculations of the values of the concentrations of free (uncomplexed) Co^{2+} and Cu^{2+} were obtained from the data given in Fig. 4, whereas the concentration of free Co^{3+} ions was calculated from the expression of the stability constant of Co*dien*$_2^{3+}$:

$$\log\beta Co(dien)_2^{3+} = \frac{[Co(dien)_2^{3+}]}{[Co^{3+}][dien]^2} \tag{12}$$

$$[Co^{3+}] = \frac{[Co(dien)_2^{3+}]}{\log\beta_{Co(dien)_2^{3+}}[dien]^2} \tag{13}$$

The difference between the potentials of cobalt(III)/cobalt(II) and copper(II)/copper systems determining the possibility to reduce copper(II) ions by cobalt(II) is negative, when the solution pH ranges from 5.0 to 9.5 (Fig. 5 b). It implies that in this pH range, copper(II)–*dien* complex reduction to metal copper by cobalt(II)–*dien* complex should take place, whereas at lower or higher pH values, a reverse process could take place, i. e. the oxidation metallic copper to Cu(II) by Co(III)–*dien* complex is

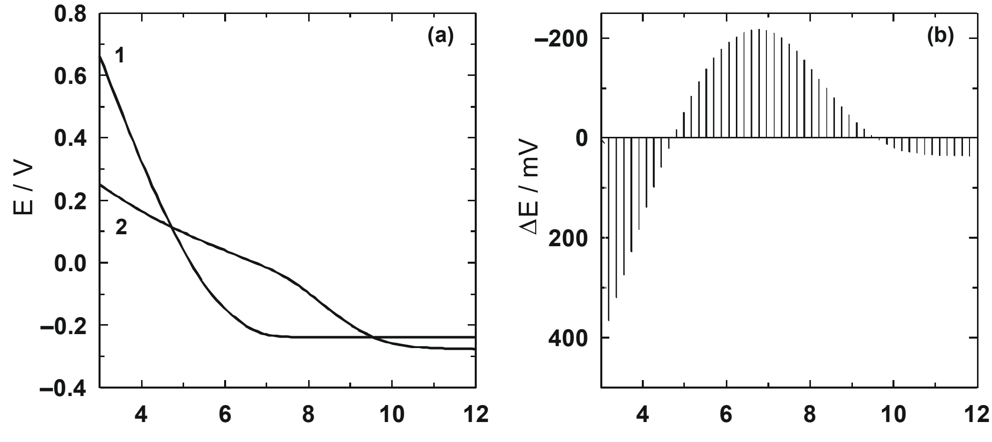

Fig. 5. The dependence of Co(III)/Co(II) (1) and Cu(II)/Cu (2) redox potentials (a) and their difference (b) on solution pH. Solution contained (mol l^{-1}): Cu(II) – 0.05, Co(II)+Co(III) – 0.15, *dien* – 0.6, Co(III) – 1% of Co(II)+Co(III) concentration. 20 °C

predicted. The largest negative difference between the redox potentials (around –0.2 V) is observed when the solution pH is ca. 7. Consequently, in the solution of this pH the highest change in free energy of copper(II) reduction by cobalt (II) is exhibited, and the reduction process should be most effective.

Therefore, the stoichiometry of the autocatalytic Cu(II) reduction by Co(II) in the *dien* solutions at lower pH (less than 7) limit can be described by this equation:

$$\mathrm{Cu}\mathit{dien}^{2+} + 2\mathrm{Co}\mathit{dien}^{2+} + \mathit{dien} \rightarrow \mathrm{Cu} + 2\mathrm{Co}\mathit{dien}_2^{3+} \quad (14)$$

However, when the solution pH is over 7, the stoichiometry is described by the following equation:

$$\mathrm{Cu}\mathit{dien}_2^{2+} + 2\mathrm{Co}\mathit{dien}_2^{2+} \rightarrow \mathrm{Cu} + 2\mathrm{Co}\mathit{dien}_2^{3+} + 2\mathrm{dien} \quad (15)$$

Thermodynamic parameters of copper reduction by cobalt are rather different from the analogous parameters of ethylenediamine system [5]. However, our experiments with the *dien* system were performed under the same conditions as the experiments with the ethylenediamine system. Consequently, the results of the thermodynamic analysis of both systems can be compared. It was found that in the case of the ethylenediamine system, the pH interval where the reduction of copper(II) takes place is wider and there is no upper pH limit. Furthermore, in the ethylenediamine system the difference between the redox potentials of Co(III)/Co(II) and Cu(II)/Cu redox couples is more considerable, when compared to the system of *dien*.

The thermodynamical predictions were confirmed by the EQCM experiments in real systems of electroless copper plating using Co(II)–*dien* complexes as reducing agents. EQCM measurements under open-circuit conditions provided information on the kinetics of copper film formation and instantaneous copper deposition rate found respectively from integral (Fig. 6a) and differential (Fig. 6b) quartz oscillator's frequency changes, and on a mixed potential of Cu electrode (Fig. 6c). The possibility to determine the instantaneous kinetic parameters seems to be especially valuable in this case due to the difficulties in obtaining such information by other experimental methods, e. g., the classical electroless copper deposition can be controlled continuously by measuring hydrogen evolution rate. The electrode mass gain in chloride-based electroless copper plating solutions under open-circuit conditions is demonstrated by the data presented in Fig. 6a, 6b. The Cu deposition rate depends considerably on the solution pH and the changes over time. The plating rate decreases with time (Fig. 6b). After ca. 1 min the system reaches quasi-stationary conditions with only small changes in E_m and copper deposition rate. The measurements of the electroless copper deposition rate in chloride solutions at pH over 5.5 are less reliable due to some Cu(II) reduction to metal in the solution volume. Stable systems were obtained by using other Cu(II) and Co(II) salts: sulfates, acetates, tetrafluoroborates [21].

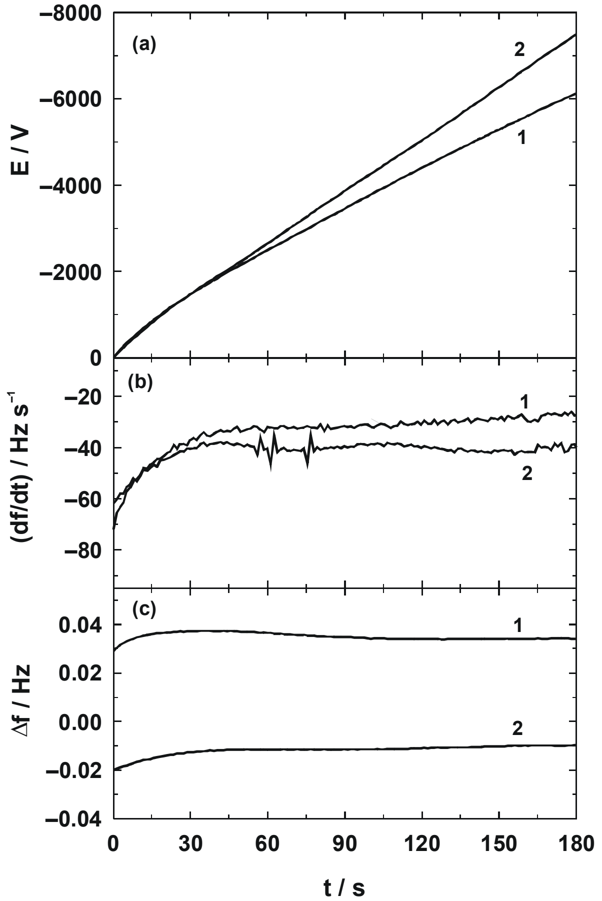

Fig. 6. Kinetics of electroless copper plating in chloride-based solution: (a) change in quartz oscillator frequency; (b) frequency change rate, (c) open-circuit potential. Solution contained (mol l^{-1}): $\mathrm{CuCl_2}$ – 0.05, $\mathrm{CoCl_2}$ – 0.15, *dien* – 0.6. Solution pH: 1 – 5.0, 2 – 5.5. 20 °C

CONCLUSIONS

1. The thermodynamic analysis of equilibria in the system Cu–Cu(II)–Co(II)–Co(III)–*dien* showed the possibility of copper(II) ion reduction to metal in acidic, neutral and alkaline solutions (at pH 5–9.5 at 20 °C).

2. The autocatalytic Cu deposition was observed under conditions where the difference between the potentials of Co(III)/Co(II) and Cu(II)/Cu redox couples was negative. The metal deposition process on the surface to be plated in the absence of the reduction reaction in the solution bulk occurs at potentials not far from the equilibrium Cu(II)/Cu potentials (at overvoltage from –5 to –50mV).

3. Co(II)–*dien* complexes are very active in copper(II) reduction, and high process rates can be obtained.

ACKNOWLEDGEMENTS

We would like to thank Dr. E. Gaidamauskas for helpful discussions and support.

Received 9 February 2007
Accepted 27 February 2007

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VARIO(II) REDUKCIJOS KOBALTO(II)-DIETILENTRIAMINO KOMPLEKSAIS PROCESO TERMODINAMINIAI ASPEKTAI

Santrauka

Co(II) kompleksai su dietilentriaminu (dien) yra gana stiprūs reduktoriai, gebantys redukuoti vario jonus iki metalo, todėl naudojami cheminės metalizacijos sistemose vario dangoms gauti. Buvo atlikta termodinaminė sistemos Cu–Cu(II)–Co(II)–Co(III)–dien analizė ir nustatytos vario(II) redukcijos kobaltu(II) sąlygos. Cu(II) redukcija vyksta pH diapazone nuo 5 iki 9,5 (20 °C). Redukcijos procesas labai priklauso nuo tirpalo pH ir ligando (dien) koncentracijos. Neigiamiausias redox potencialų skirtumas (ΔE) tarp Cu(II)/Cu ir Co(III)/Co(II) poros siekia –200 mV. Didžiausias metalo nusodinimo greitis gautas tirpaluose, kuriuose vyrauja Co*dien*$^{2+}$ ir Co*dien*$_2^{2+}$ kompleksai.