Autocatalytic copper(II) reduction by cobalt(II)–ethylenediamine complex studied by rotating disc electrode technique

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The autocatalytic copper(II) reduction by cobalt(II) in ethylenediamine solutions (electroless copper plating) was studied on a rotating disk electrode by potential and copper deposition rate measurements. The Cu(II) reduction process depended largely on anions present in plating solution; the process rate decreased in a sequence: chloride, tetrafluoroborate, nitrate, sulphate. The process in sulphate and nitrate solutions can be effectively accelerated by addition of bromide on a mM level. The copper(II) reduction process is under a mixed chemical and mass transfer control. By increasing the desk electrode rotation rate the copper deposition can be accelerated up to twofold. The copper deposition rate increases sharply at even a slow plating solution movement; the process acceleration is explained by a removal of the inhibiting reaction product – cobalt(III) species weakly bound to copper surface.

Key words electroless copper plating, cobalt(II)–ethylenediamine complexes, rotating disk electrode

INTRODUCTION

The cobalt(II) complex with ethylenediamine (En) was found [1] to be an effective reducing agent in the autocatalytic reduction of copper(II) to metal (electroless copper plating) Thermodynamic analysis and kinetic investigations were carried out for the copper deposition in this system [2–6], and a rather high rate of reduction process on the metal surface without 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 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.

The recent electrochemical investigation of the autocatalytic process of copper(II) reduction by cobalt(II)–En complex [7] showed that copper deposition resulted from coupling of partial electrochemical reactions of Cu(II)–En reduction and Co(II)–En oxidation occurring simultaneously on copper surface. Some deviations from partial reactions additivity were found and explained by differences in the ligand (En) concentration at the catalytic surface in separate Cu(II) and Co(II) solutions and in the total electroless plating system; no great non-additivity effects typical of the classical electroless plating systems (Cu(II)–formaldehyde, Ni(II)–hypophosphite) were observed.

Stirring of the electroless copper plating solutions has a great effect on copper deposition: at the solution flow with a comparatively low rate (wall-jet cell) the copper plating rate was *ca*. 10-fold higher compared to that in a stationary (unstirred) solution [7]. Chloride ions were found to play an important role in facilitating the autocatalytic copper reduction process; all halide ions enhance cobalt(II)–En complex anodic oxidation on copper [8].

The aim of the present study was to continue the investigation of Cu(II)–En reduction by Co(II)–En, especially under controlled mass transfer conditions, using a rotating disk electrode and to study anion effects on this process.

EXPERIMENTAL

A rotating disk electrode, copper deposition rate and potentiometric measurements were used to study the Cu-Cu(II)–Co(II) system in En solutions.

A 0.25 cm^2 platinum rotating disc electrode was used as a substrate for electroless copper plating. In some experiments the platinum disc electrode was plated with a thin layer of copper from an electroless bath containing Co(II)–En complex before each series of measurements. A closed cell was used, solutions were purged with Ar before introducing Co(II) to avoid oxidation by atmospheric oxygen; the Ar atmosphere was maintained over the solution during measurements. The potential was measured with respect to the $Ag|AgCl|KCl_{sat}$ RE, and its values are given *vs.* this electrode.

The electroless copper deposition rate was determined by measuring the amount of copper deposited on the rotating disc in 15 min. The copper deposit was dissolved in HNO_3 (2:1), and the solution was diluted to 50 ml with distilled water; to several ml of this solution 5 ml H_2SO_4 (1:1) and 2 ml solution of Na diethyldithiocarbamate (1 g/l in 0.1 M NaOH) were added and diluted to 50 ml. The optical density of the solution was measured at a wavelength λ = 454 nm using a Perkin–Elmer *Lambda* 35 UV/VIS spectrometer, and the copper(II) concentration was found from the calibration graph (Fig. 1); the calibration graph was checked periodically because of some changes in optical density connected with the aging of the diethyldithiocarbamate solution.

The electroless copper plating solutions contained (M): Cu(II) – 0.05, Co(II) – 0.15, ethylenediamine – 0.6. Four types of plating solutions containing different anions – (chloride, sulphate, nitrate and tetrafluoroborate) were used; the corresponding salts of Cu(II) and Co(II) were dissolved for their preparation. Solution pH was adjusted to approx. 7 (the exact pH value was selected for each solution type

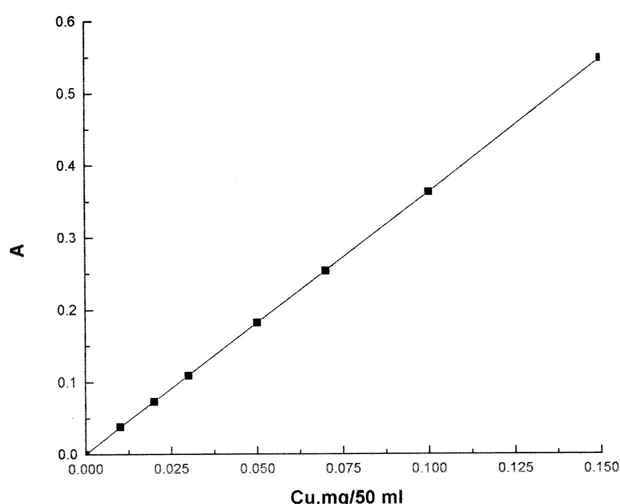

Fig. 1. Calibration graph of spectropgotometric copper(II) determination using diethylduthiocarnamate complex. λ = = 454 nm

to ensure the best solution stability) by adding the acid with the necessary anion. The copper plating solution preparation procedure was as follows: to distilled water the solutions of copper salt, ethylenediamine and acid were added, the solution was deaerated by Ar and cobalt(II) salt solution was added under inert atmosphere. Reagent grade chemicals and bidistilled water were used to prepare the solutions, except for cobalt(II) tetrafluoroborate: its solution was prepared from cobalt(II) nitrate by precipitating cobalt(II) hydroxide, washing and dissolving it in HBF_4. All experiments were carried out at 20 ± 1 °C.

RESULTS AND DISCUSSION

Copper(II) reduction by cobalt(II) complexes is very sensitive to solution pH. Therefore, for studying mass transfer and anion effects, an approximately constant pH value was selected – *ca*. 7. Such solutions were investigated in our previous study [7] using other experimental methods, and the data of this work can be compared with those of [7]. The pH value chosen ensures a satisfactory plating solution stability and a rather high copper deposition rate in the basic chloride-containing solution.

Measurements showed that electroless copper deposition took place at the open-circuit potentials more negative than *ca.* –0.3 V (*vs.* silver chloride reference electrode). The open-circuit potential of a copper or platinum electrode can therefore be an indication of the autocatalytic copper deposition process.

The autocatalytic copper(II) reduction by cobalt(II) began spontaneously on the rotating platinum disk electrode in chloride-containing electroless copper plating solutions only; in the case of other (nitrate, sulphate, tetrafluotoborate) solutions the plating process can be initiated by adding an accelerator – bromide ions. Bromide introduced even at a level of 0.1 mM shifts the platinum electrode potential to more negative values by 30–80 mV (Fig. 2), and copper deposition begins. The Pt electrode response to bromide ions depends on the anion present in solution: in nitrate solutions the electrode potential shifts to considerably more negative values and platinum is covered by copper film, in contrast to terafluoroborate-containing solutions where the bromide effect was much lower and the copper deposition was rather slow, a complete coverage of Pt surface by copper was obtained in 10–20 min. It is necessary to note one more difference in the response to bromide addition between NO_3^- and BF_4^- solutions: while copper electrode behaviour in nitrate solution is practically identical to that of platinum electrode (curves 1 and 2 in Fig. 2), in

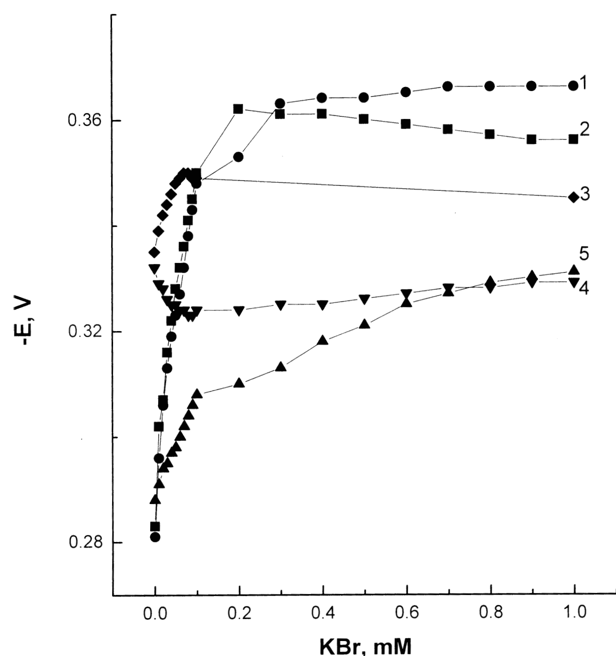

Fig. 2. 9. Dependence of rotating disc electrode potential on bromide addition to electroless copper plating solution. Solution contained (M): Cu(II) – 0.05, Co(II) – 0.15, En – 0.6; pH: 6.9 (*3*), 7.1 (*1, 2, 4, 5*). Anion in the solution: nitrate (*1, 2)*, chloride (*3*), tetrafluoroborate (*4, 5*). Electrode: Cu (*1, 3, 4*), Pt (*2, 5*). Electrode rotation rate (rpm): 350 (*1, 2, 4, 5*), 4600 (*3*)

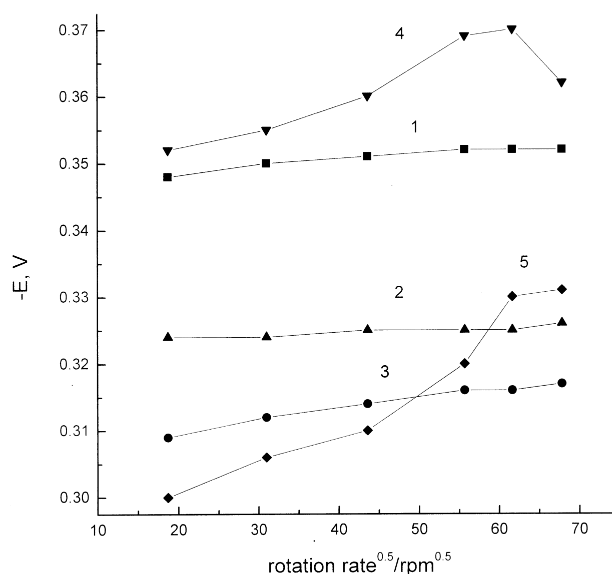

Fig. 3. Dependence of rotating disc electrode potential on rotation rate. Solution contained (M): Cu(II) – 0.05, Co(II) – 0.15, En – 0.6; pH: 6.9 (*4*), 7.1 (*1– 3, 5*). Anion in the solution: nitrate (*1)*, tetrafluoroborate (*2,3*), chloride (4), sulphate (*5*). Electrode: Cu (*1, 2, 4, 5*), Pt (*1, 3*). Bromide concentration (mM): 0 (*4*), 0.1 (*1 – 3*), 10 (*5*)

tetrafluoroborate solution the Cu potential is negative enough for the autocatalytic copper ion reduction in the absence of bromide (*ca.* –0.33 V) and bromide addition doesn't shift the Cu potential to mote negative values, instead it becomes slightly more positive (curve 4 in Fig. 2). The bromide ion seems to have some accelerating effect in chloride solutions – the copper potential becomes more negative on adding 0.1–0.2 mM of bromide (curve 3 in Fig. 2) with returning to less negative values at higher bromide concentrations. Bromide concentrations over 1 mM do not change appreciably the electrode potential in either of the solution studied and apparently have no additional effect on the catalytic process.

The data presented above demonstrate a variety of anion effects on Cu(II) reduction by Co(II). Chloride ensures an effective copper ions reduction, while nitrate and sulphate solutions are rather inert and the autocatalytic reduction process in them can be enhanced by a small addition of bromide; BF_4^- presents one more case with some reduction process on copper surface and no sensitivity to bromide ion addition.

The electrode rotation rate has some influence on the electrode potential, higher rates leading to more negative potential values in general (Fig. 3). The potential changes at changing the rotation rate are almost negligible for Cu in BF_4^- solutions, they are slightly higher (up to 10 mV for Pt in BF_4^- solution and both Cu and Pt in nitrate solution). More pronounced potential changes were observed for chloride and sulphate copper plating solutions – ca. 20 and 30 mV, respectively. But at the highest electrode rotation rates (*ca.* 4000 rpm) the copper potential in these solutions is either does not change (sulphate) or even shifts to more positive values (chloride) with increasing rotation intensity.

The electroless copper deposition rate increased with rising the electrode rotation rate (Fig. 4). In chloride solutions, the high accelerating effects of electrode rotation were observed both at low and high rotation rates (400–900 and 2500–3500 rpm), the copper plating rate even decreasing at the highest rotation rates. The total acceleration of copper deposition process in these solutions is more than twofold – the plating rate increases from 0.5 to 1.2 mg/0.25 cm^2 in 15 min. For sulphate solutions containing bromide ion additive, a more significant acceleration of copper deposition was observed only at high electrode rotation rates.

Although an extrapolation of the dependences 'deposition rate – $\omega^{1/2}$' to zero rotation rate for such a complicated process as the autocatalytic copper deposition consisting of two coupled electrochemical reactions had no strict theoretical foundation, it would produce the finite copper deposition rates – *ca.* 0.2 mg for the sulphate solution and *ca.* 0.4 mg

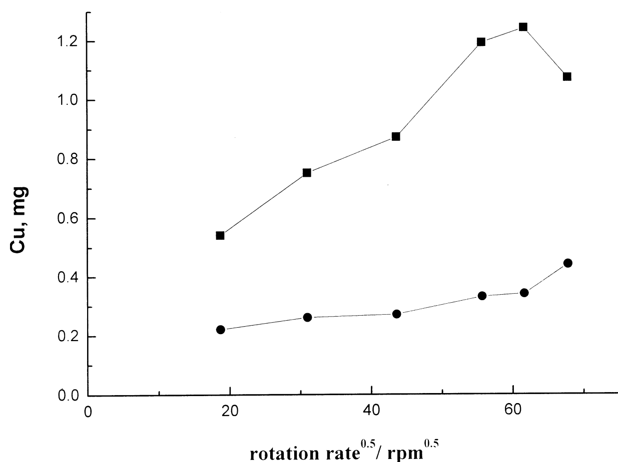

Fig. 4 Dependence of electroless copper deposition rate on electrode rotation. Solution contained (M): Cu(II) – 0.05, Co(II) – 0.15, En – 0.6; pH: *1* – 6.9, *2* – 7.1. Anion in the solution: chloride (1), sulphate (*2*). Bromide concentration (mM): 0 (*1*), 10 (*2*)

for the chloride one. The data presented seem to indicate that the processes studied are under a mixed chemical and mass transfer control. The situation seems to be similar to that of cobalt(II)–En complex anodic oxidation on silver and gold [9, 10]. Only a limited role of mass transfer in these processes is compatible with the rather high concentrations of the reacting species – cobalt and copper complexes.

On the other hand, the information available (results presented in [7, 8] and obtained in this study) gives an opportunity to discuss the specific aspects of the autocatalytic process mechanism in relation to mass transfer effects, especially at the lowest and highest electrode rotation (solution flow) rates.

In the previous study [7], the electroless copper deposition rate from the same chloride-type solution as studied in this work was determined by EQCM to be *ca*. 1 mA/cm^2 in stationary conditions (unstirred solution) and *ca*. 10 mA/cm^2 in flow-through conditions (wall-jet cell). The present investigation gave for the average copper deposition rate in 15 min, when expressed in current density units, 7–16.5 mA/cm^2 for the whole range of disk electrode rotation rates. Having in mind the different rate measurement methods – the instantaneous copper deposition rate was measured at an initial moment and the process rate usually falls in time (the average rate for 15 min probably will be lower), the wall-jet cell results correspond to those obtained at disk rotation rates *ca*. 1000 rpm or less. But the copper deposition rate at stationary conditions seems to be in contradiction to the data obtained on a rotating disk electrode. The expected value for copper deposition rate at zero rotating rate given earlier – ca. 0.4 mg cm^2 for 15 min, corresponding to 5.5 mA/cm^2, is incomparable to 1 mA/cm^2 obtained experimentally by EQCM as an instantaneous rate. Apparently, copper(II) reduction by cobalt(II) proceeds quite differently in stationary conditions and at solution flow even at low flow rates. The considerably lower copper deposition rate in absence of solution movement is explained bt an inhibiting action of a reaction product – cobalt(III) species which were shown [7] to remain at the catalyst surface an can be reduced at more negative electrode potentials. These Co(III) compounds are weakly bound to copper surface and removed by solution movement; for such a removal the disk rotation rate of 360 rpm is enough.

The other unusual feature of the electroless copper deposition process is a change of the plating rate – disk rotation rate dependence type at the highest electrode rotation rates. The copper plating rate is not growing further with the rotation rate or even falls down as is shown by both deposition rate and copper open-circuit potential measurements in chloride solutions (Figs. 3 and 4). This effect may be related to the removal of adsorbed reacting species from the copper surface; the transportation of the reducing agent, cobalt(II) compounds, is more probable since the potential shift to less negative values is observed. Earlier a decrease of autocatalytic nickel deposition process rate at high disk electrode rotation rates was observed in the Ni–N(II)–hypophosphite system [11], which also can be explained by removal of the adsorbed reducing agent or its oxidation intermediates from the catalyst surface.

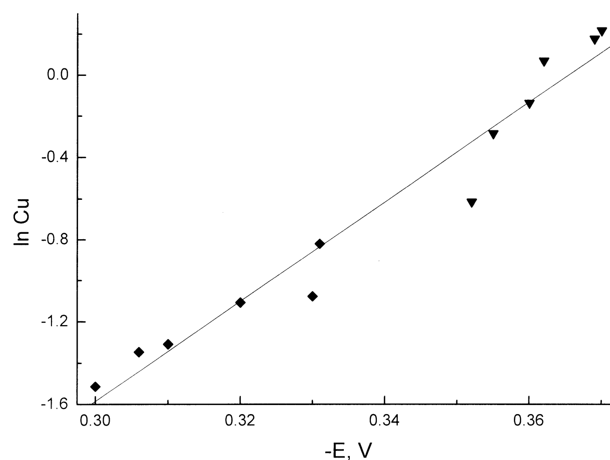

Fig. 5. Semi-logarithmic plot of electroloess copper deposition rate vs. pot4ential for various electrode rotation rates. Plating solutions contained chloride (▼) and sulphate (♦). Data were taken from Figs. 3 and 4.

From copper deposition rate and copper open-circuit potential data (Figs. 3 and 4) the volt-ampere dependence can be constructed for copper deposition from chloride and sulphate solutions. Such construction is valid in the case of electrochemical mechanism of the autocatalytic process; this seems to be proved earlier [7]. The resulting volt-ampere dependence (Fig. 5) for both chloride and sulphate solutions can be described by one exponential curve, showing that changes in the autocatalytic process rate at different electrode rotation rates and in the presence of different anions occur only or mostly as a result of changes in anodic cobalt(II) oxidation process, and the cathodic Cu(II) reduction is changing little.

CONCLUSIONS

1. The autocatalytic reduction of Cu(II)–En by Co(II)–En complexes depends largely on anions present in the plating solution; the process rate decreases in a sequence: chloride, tetrfluoroborate, nitrate, sulphate. The reduction process in nitrate and sulphate solutions can be effectively accelerated by adding 0.1–1 mM bromide.

2. The electroless copper plating can be accelerated more than twofold by increasing the disk electrode rotation rate. The reduction process is under a mixed chemical and mass transfer control.

3. Even a slow plating solution movement rises the copper deposition rate up to tenfold compared to the stationary solution; the effect is explained by a removal of the inhibiting reaction product – cobalt(III) species weakly bound to the catalytic surface.

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AUTOKATALIZINĖS VARIO(II) REDUKCIJOS KOBALTO(II) KOMPLEKSAIS TYRIMAS TAIKANT SUKAMĄ DISKO ELEKTRODĄ

S a n t r a u k a

Potencialo ir vario nusėdimo greičio matavimai sistemose Cu-Cu(II)-Co(II)-etilendiaminas (En) ir PT-Cu(II)-Co(II)--En parodė, kad autokatalizinė vario jonų redukcija kobalto(II) kompleksais (cheminis variavimas) labai priklauso nuo tirpale esančių anijonų. Vario nusėdimo greitis mažėja eilėje: chloridas, tetrafluoroboratas, nitratas, sulfatas; vario jonų redukciją nitratų ir sulfatų tirpaluose efektyviai greitina nedideli bromido priedai.

Didinant disko elektrodo sukimo greitį galima daugiau kaip 2 kartus pagreitinti variavimą, kurio greitį nulemia tiek cheminiai, tiek masės pernešimo procesai. Vario nusodinimą nejudančiame tirpale labai pagreitina net lėtas tirpalo judėjimas; šis efektas paaiškinamas tuo, kad tirpalo srautas pašalina redukcijos procesą stabdančius reakcijos produktus – kobalto(III) junginius, nestipriai surištus su vario paviršiumi.