Investigation of the processes and mechanism of electrodeposition of copper from ammonium nitrate electrolyte by the method of cyclic voltamperometry

L. N. Petkov*, K. N. Ignatova

University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., Sofia 1756, Bulgaria

This article reports results, obtained by the method of cyclic voltamperometry, applied to study the processes and mechanism of deposition of copper from ammonium nitrate electrolyte. The effect of the initial potential has been studied as well as that of the potential sweeping rate and the nature of the cathode substrate (copper or silver) in regard to the course of the voltamperograms. It has been established that the deposition of copper on a copper substrate is proceeding via two-step mechanism, whereupon the elemental copper is obtained by reduction of cuprous ammonium ions. Upon applying the diagnosis criteria of the method it was confirmed that the mechanism corresponds to the Electrochemical-Chemical-Electrochemical (EChE) type i.e. two consecutive reversible electrochemical steps (cupric/cuprous ammonium complexes and cuprous ammonium complexes/elemental copper), with an intermediate chemical step of copper disproportionation. In case of silver substrate, only the mechanism of the anodic process is relatively the same. The ascertained difference in the mechanisms of copper deposition is very important for the combined deposition of copper and silver and for obtaining Ag-Cu alloyed coating, taking into account the fact that silver is the more electropositive metal in the system. The obtained results are an essential part of an extensive study, connected with preparing an alloyed finely dispersed Ag-Cu powder under stationary conditions and in impulse potentiostatic regime.

Keywords: Cu powder, cyclic voltamperometry, ammonium nitrate electrolyte.

INTRODUCTION

The electrolysis is a method, enabling to prepare directly alloyed metal powders of high purity and compositions varying within wide limits [1–3]. The applying of an impulse potentiostatic regime enriches considerably the options in this respect. In this case the investigation of the mechanism of the processes of separate deposition of the metals in detail is extremely important, as upon applying a potentiostatic impulse there is a continuous transition from zero to very high values of the over-potential. All the steps of the mechanism of the occurring processes are reflected on the quality of the final product [2–5].

The alloyed Ag–Cu powders are valuable in view of their electroconductivity and thermal conductivity properties. They are used mainly for improving the electroconductivity of contacts in the electronics and also for components of pastes for depositing on metal surfaces before their soldering [6, 7]. Nevertheless data on the conditions of deposition are scarce. Our preliminary work [8] concerns alloyed Ag-Cu powders.

After studying a series of electrolytes the ammonium electrolyte for copper deposition became of fundamental interest, taking into account the fact that the copper in it is available in two different soluble forms: the cupric Cu^{2+} and cuprous Cu^+ ammonium complexes. However only a few articles [9 – 12] are devoted to this system. Some of them investigate the influence of pH and that of some anions like Cl^- [9–11] or NO_3^- [10] at very low concentrations of the copper. These are focused on the mechanism of formation of nuclei of copper crystals. It has been shown that the NO_3^- ions can dissolve partially the growing copper crystal nuclei. Another investigation points out that the NO_3^- ions (e.g. originating from NH_4NO_3) not only promote the electroconductivity of the solution but they can also adsorb on the electrode surface thus facilitating the electrodeposition of copper ions. In most of the studies the copper is introduced in the form of $CuSO_4$ [13–19]. The most detailed data on the mechanism of electrodeposition are represented in the article [12], where the application of the method of cyclic chronovoltamperometry is combined with physical methods and a specific mechanism of copper deposition is proposed for the various pH regions (pH = 4, 6 and 8).

The complete analysis of the literature data imposes the conclusion that the ammonium electrolyte with an additive of ammonium nitrate is

---

* To whom all correspondence should be sent:
E-mail: l.petkovv@abv.bg

especially appropriate for the combined deposition of copper and silver in the form of alloyed coating or powder, especially when ammonia is in moderate excess (pH about 8.5–9). In all the other electrolytes: sulfuric acid [12], pyrophosphate [20], fluoroborate [21], trionate [22], alkaline [23], etc. the silver forms hardly soluble compounds and the electrolytes on their basis are unstable.

On the basis of the above arguments a composition of the electrolyte was chosen, in which the copper is in the form of $Cu(NO_3)_2$ and its concentration was varied from 2.5 to 10 g·dm^{-3}, whereupon ammonia is added to obtain pH = 8.5–9. The method of cyclic voltamperometry was applied to electrodes of copper and silver in view of the purpose of this study. The method is especially suitable for complex systems such as those, in which there is a two-step transfer of electrons and ions of changing valence, which form complexes completely different in stability. The elaborated diagnosis criteria of the method [24–26] allow a strict and detailed evaluation of the occurring processes. These criteria originate from the basic equations of the method. They represent the dependences of the deviation of the cathode potential E_p^c, the relationship between the currents, corresponding to the anode and cathode maxima (I_p^a/I_p^c), as well as the ratio of the cathode current in the position of the peak and the square of the rate of sweeping the potential v. It is obvious that depending on the specific mechanism of the process, for which the above parameters have been calculated, the values will be quite different.

EXPERIMENTAL

The electrolyte, in which the studies have been carried out, has the composition: 2.5 g·dm^{-3} Cu (in the form of $Cu(NO_3)_2$); 40 g·dm^{-3} NH_4NO_3 solution and 25% NH_3 solution to obtain pH = 8.5–9. The salts are both added consecutively to the water and as they are both well soluble in water, there are no substantial peculiarities in this step of solution preparation. There follows a gradual addition of ammonia, whereupon the solution becomes dark at pH = 7–8. The addition of ammonia to reach pH = 8.5 and further pH = 9 makes the solution trans-parent, blue-colored, which is an indication of the formation of cupric ammonia complex $[Cu(NH_3)_4]^{2+}$ [27].

The measurements have been carried out in a three-electrode cell with working electrodes, made of copper (99.97%) and silver (96.97%), in the form of disks with working area 1 cm^2. Platinum net was used as anode, while the reference electrode was saturated calomel electrode (SCE).
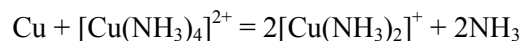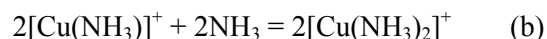
The cyclic chronovoltamperograms have been recorded by means of potentio-scanner of the type "Wenking" (Germany) in the range of potentials 0.450 V ÷ –0.800 V (*versus* SCE). The polarization was always carried out starting from the chosen initial potential and moving towards more negative potentials. The curves, which are represented in the figures in this article, have been obtained after several cycles (4 to 5 cycles). The sweeping rate of the potential was varied in the range from 10 to 150 mV·s^{-1}. The rate, at which the peculiarities of the mechanism of copper deposition are best demonstrated, was found to be $v = 20$ mV·s^{-1}.

RESULTS AND DISCUSSION

Values of the potentials of the electrochemical reactions

In order to facilitate the analysis of the results all the basic reactions, which could possibly occur in the working electrolyte, as well as their standard potentials versus NHE, are represented in Table 1. The table lists also the calculated values of the reversible potentials in the reactions with respect to SCE [27].

An assumption has been made, during the calculation of the potentials of the reactions (1) and (3), that the copper disproportionation reaction is occurring according to the following equations:

$$Cu + [Cu(NH_3)_4]^{2+} = 2[Cu(NH_3)]^+ + 2NH_3 \quad (a)$$

$$2[Cu(NH_3)]^+ + 2NH_3 = 2[Cu(NH_3)_2]^+ \quad (b)$$

$$Cu + [Cu(NH_3)_4]^{2+} = 2[Cu(NH_3)_2]^+ + 2NH_3$$

Another assumption is that the constant of disproportionation, in accordance with the literature data [28], is equal to:

$$K = \frac{\left[Cu(NH_3)_2^+\right]^2}{\left[Cu(NH_3)_4\right]^{2+}} = 6.04 \cdot 10^{-7} \quad (7)$$

During the calculations it has been accepted for the concentration of $[Cu(NH_3)_4]^{2+}$ that the free cupric ions are entirely bonded in an ammonia complex i.e. it is 2.5 g·dm^{-3} (or 0.0393 M).

Cyclic voltamperometry of copper–ammonium nitrate electrolyte

Voltamperograms on copper electrode. Figure 1 represents the voltamperogramme of copper-ammonium nitrate electrolyte in the interval of potentials from $E_i = -0.200$ V to $E_c = -0.750$ V.

Table 1: Standard potentials of the basic reactions in ammonium nitrate electrolyte for the deposition of copper (E_0) with respect to SVE, as well as the values of the potential of these reactions (E) in regard to RCE, recalculated on the basis of the equation of Nernst.

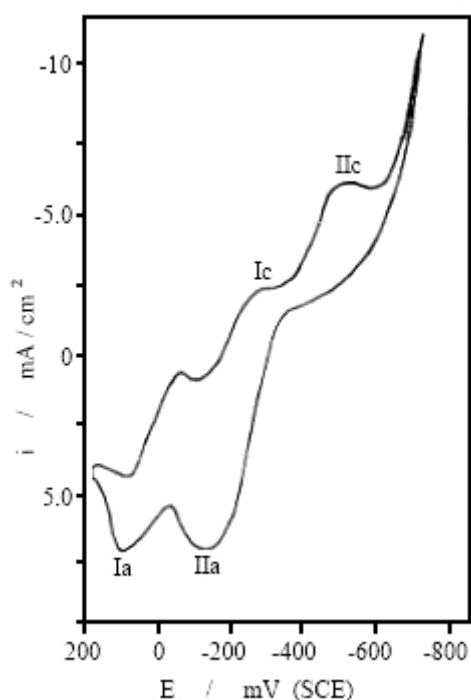| No.	Reaction	E°, V [NHE]	E_{calc}, V [SCE]
(1)	$[Cu(NH_3)_4]^{2+} + e^- = [Cu(NH_3)_2]^+ + 2NH_3$	–0.010	–0.115
(2)	$Cu + [Cu(NH_3)_4]^{2+} = 2[Cu(NH_3)_2]^+ + 2NH_3$		
	Copper disproportionation reaction		
(3)	$[Cu(NH_3)_4]^{2+} + 2e^- = Cu + 4NH_3$	–0.050	–0.334
(4)	$[Cu(NH_3)_2]^+ + e^- = Cu + 2NH_3$	–0.120	–0.586
(5)	$NO_3^- + 5H_2O + 6e^- = NH_2OH + 7 OH^-$	–0.300	–0.085
(6)	$[Ag(NH_3)_2]+ + e^- = Ag + 2NH_3$	0.373	0.034
	(for $C_{Cu} = 2.5$ g·dm^{-3} and $C_{Ag} = 2.5$ g·dm^{-3})		

Fig. 1. Voltamperogramme of copper-ammonia nitrate electrolyte on copper electrode; 2.5 g·dm^{-3} Cu in the form of Cu(NO$_3$)$_2$, (40 g·dm^{-3} NH$_4$NO$_3$ and 25% NH$_3$ until pH = 9 is reached); E_i = +0.200 V, E_c = –0.750 V, v = 20 mV·s^{-1}.

As it can be seen from the figure two consecutive cathode peaks are observed on the voltamperogramme – Ic and IIc and their corresponding anode peaks IIa and Ia. The first cathode peak, as it follows from the data represented in Table 1, is associated with the reduction of cupric ammonium ions $[Cu(NH_3)_4]^{2+}$ into cuprous ammonium ions $[Cu(NH_3)_2]^+$ in accordance with the stoichiometric Eqn. (1):

$$[Cu(NH_3)_4]^{2+} + e^- = [Cu(NH_3)_2]^+ + 2NH_3 \quad (1)$$
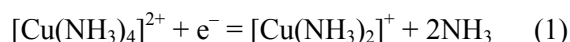
As our visual observations in this field of potentials show, no elemental copper has been deposited. When the equilibrium concentration is reached, the obtained cuprous ammonium ions $[Cu(NH_3)_2]^+$ are immediately involved in the reaction of disproportionation (2), which in this case is the following:

$$[Cu(NH_3)_4]^{2+} = 2[Cu(NH_3)_2]^+ + 2NH_3 \quad (2)$$

This reaction does not lead to a peak in the current, but it rather contributes to the preservation of the current intensity value on a certain level. In the region of the second cathode peak IIc the cupric ammonium ions $[Cu(NH_3)_4]^{2+}$ are reduced to elemental copper following the stoichiometric equation (3):

$$[Cu(NH_3)_4]^{2+} + 2e^- = Cu + 4NH_3 \quad (3)$$
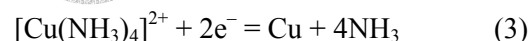
It is not probable that the deposition of elemental copper could occur via reduction of cuprous ammonium complexes $[Cu(NH_3)_2]^+$ in the studied electrolyte, containing a sufficient surplus of ammonia, which forms stable complexes with the divalent copper ions. In fact the calculations, which we performed (Table 1), point to the fact that this reaction is possible, but it occurs at higher cathodic potentials, compared to reaction (3).

As it follows from Figure 1 the first anodic peak (in the order of appearance upon returning the curve to the initial potential) IIa appears at about –0.150 V (SCE) and it is weakly dependent on the sweeping rate of the potential. It is connected with oxidation of the deposited copper coating via the reaction:

$$Cu + 4NH_3 = [Cu(NH_3)_4]^{2+} + 2e^- \quad (4)$$
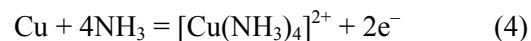
In the next step the cupric ammonia ions $[Cu(NH_3)_4]^{2+}$, located most closely to the electrode, are reduced chemically *via* reaction (2) to cuprous ammonia ions (the reaction of disproportionation).

The second anodic peak Ia appears at about 0.100 V (CE) and it is connected with the soluble forms of the copper in solution, i.e. with the reaction of oxidation of the cuprous ammonia complexes into cupric ammonia complexes, described by the stoichiometric equation:
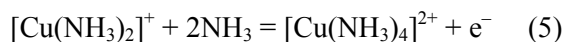
$$[Cu(NH_3)_2]^+ + 2NH_3 = [Cu(NH_3)_4]^{2+} + e^- \quad (5)$$

41

Fig. 2 (a–c) shows three cyclic voltamperometric dependences in an electrolyte of composition 2.5 g·dm^{-3} Cu; 40 g·dm^{-3} NH$_4$NO$_3$; NH$_3$ (until pH = 8.5 is reached) on copper electrode at three different values of the initial potential: 0.000, 0.100, 0.200 V. The course of the curves is an indication that the variation of the initial potential in the studied interval does not change substantially the mechanism of the entire process.

Voltamperogrammes on silver electrode. A weak initial cathodic peak is observed in the voltampero-

grammes, taken with a silver electrode in an electrolyte, containing in advance cupric ammonia ions [Cu(NH$_3$)$_4$]$^{2+}$ (Fig. 3), at more positive potentials and a stretching plateau at the more negative potentials (–0.100 V). In this case, no stepwise deposition of copper is observed, as in the case with copper electrode. It is not possible that the reaction of disproportionation of the copper can occur on a silver electrode and it has been demonstrated above that it is exactly this reaction that lies in the basis of the two-step copper deposition.
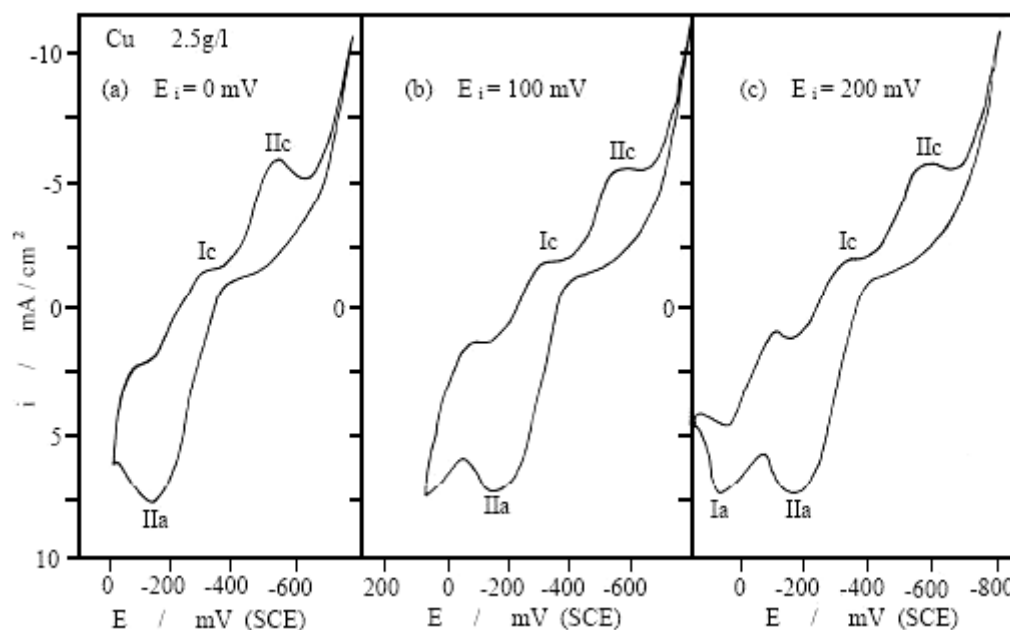

Fig. 2. Voltamperogramme of copper–ammonia nitrate electrolyte at various values of the initial potential E_i:
(a) E_i = 0.000 V; (b) E_i = 0.100 V, (c) E_i = 0.200 V; v = 20 mV·s^{-1}.
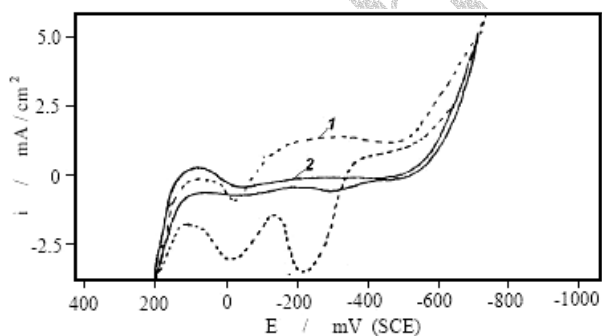

Fig. 3. Voltamperogramme of copper-ammonia nitrate electrolyte on silver electrode; E_i = 0.200 V, final potential E_c = –0.750 V, v = 20 mV·s^{-1} (curve 1).
Curve 2 is the basic electrolyte.

In the anodic region the character of the curves is not different from that on a copper electrode – two peaks IIa and Ia are observed. They are associated with the consecutively occurring reactions (4) and (5), i.e. the oxidation of the copper coating, deposited in the cathodic region.

It is obvious that on a silver electrode only the reduction of copper is occurring by a mechanism different from that on a copper substrate, which is due to obstruction of the reaction of disproportionation (6). The fact that the deposition of copper, in this case, is proceeding on a substrate of different nature, is the reason for the registered comparatively lower currents in the process of copper deposition, compared to those on a copper electrode.

Cyclic voltamperometry of a basic electrolyte. The voltamperogrammes of an electrolyte not-containing any copper ions and having a composition 40 g·dm^{-3} NH$_4$NO$_3$ and NH$_3$ (until pH = 9 is reached) represent some interest (Fig. 4). As it can be seen from the comparison with the respective dependence for solutions containing copper ions (curve 1), there exists an analogy between the peaks in the current in intensity, but those in the copper-containing solutions are higher. It can be supposed that their appearance in the basic electrolyte is owing to processes, in which copper ions are parti-

cipating. The same peaks are obtained upon cycling in anodic direction (the represented dependence is recorded after five cycles) or as a result of chemical dissolution of the copper electrode in the ammonia medium at the above-specified values of pH (8.5–9).
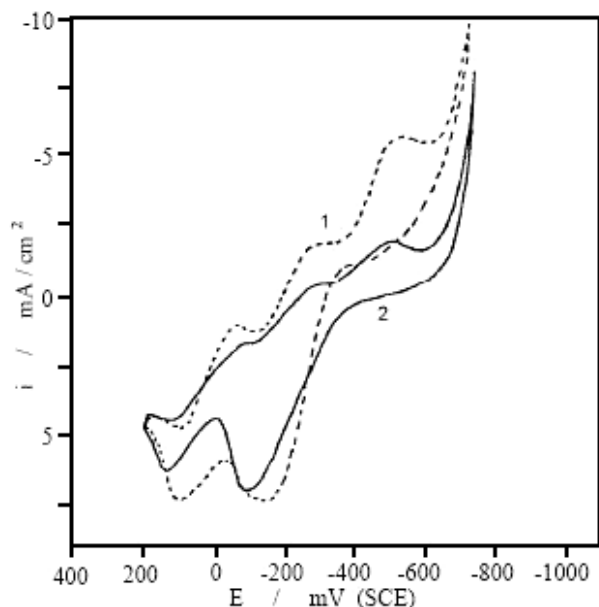

Fig. 4. Voltamperogramme of the basic electrolyte on copper electrode (40 g·dm^{-3} NH$_4$NO$_3$ and 25% NH$_3$ until pH = 9 is reached) on copper electrode (curve 2); Curve 1 is the copper containing electrolyte.

When the initial potential has a value amounting to $E_i = -0.295$ V the only occurring process is the evolution of hydrogen (Fig. 5) and no maxima in the current intensity are observed.
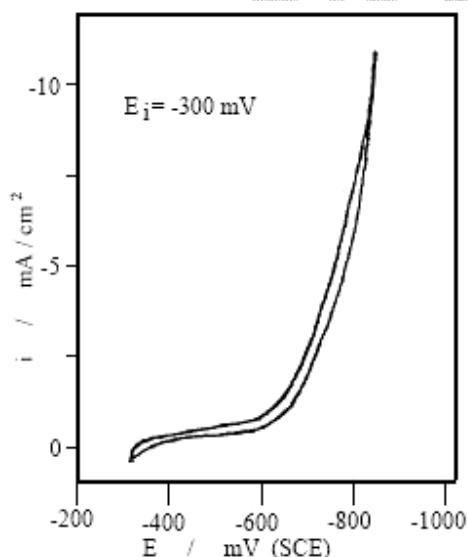

Fig. 5. Voltamperogramme of the basic electrolyte on copper electrode at initial potential $E_i = -0.300$ V.

The appearance of two consecutive cathodic peaks in the curves and the respective anodic peaks are observable in case of shifting of the initial potential in positive direction (up to 0.300 V).

Evidence in favour of the statement that the current peaks, obtained on copper electrode, are connected with the copper ions, is given by the voltamperogrammes, recorded with a silver electrode in the basic electrolyte (Fig. 6 curve 1). No current maxima are observed in the range of potentials from 0 to –0.800 V i.e. no processes are occurring in this electrolyte. Such peaks/processes are observable both in the cathodic and in the anodic direction but at potentials 0.00 – 0.400 V. These are most probably associated with the processes of formation and reduction of the silver ammonia complexes [Ag(NH$_3$)$_4$]$^+$ into Ag° – reaction (6) from Table 1.
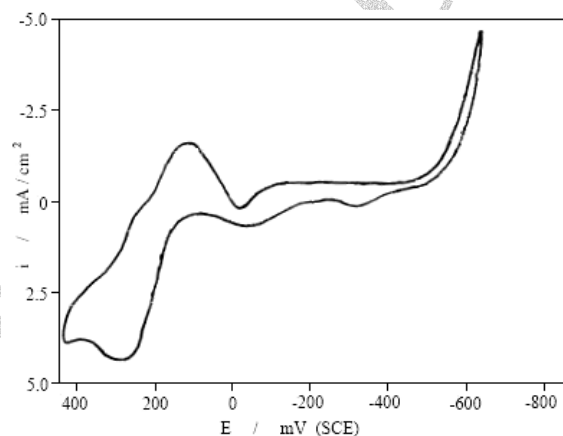

Fig. 6. Voltamperogramme of the basic electrolyte on silver electrode at initial potential $E_i = +0.450$ V.

Influence of the rate of sweeping of the potential (scan rate)

The voltamperogrammes were recorded in a copper-containing electrolyte with a copper electrode at different rates of sweeping of the potential from 20 to 150 mV·s^{-1} (Fig. 7). Both cathodic peaks and the respective anodic peaks are growing up with the increase of the rate of sweeping of the potential and they have a comparatively symmetrical character, which indicates the fact that they are connected with reversible processes.

The diagnosis criteria of the method of cyclic chronovoltamperometry [17, 18] were applied to each one of the two peaks separately (Table 2). The following was established for the first cathodic peak (Ic) and the respective anodic peak (IIa): A) The potential in the region of the cathodic peak is slightly shifted cathodically with the rate of sweeping the potential; B) The ratio $I^a_p/I^c_p > 1$ (varying from 1.32 to 1.07) and it is decreasing with the increase of the square root of the rate $\sqrt{v}$; C)

The function of the current $I_p^c/\sqrt{v}$ does not change with the increase of $\sqrt{v}$. These dependences point to the occurring of an Electrochemical-Chemical (EC) mechanism, consisting of a reversible electrochemical reaction, followed by a reversible chemical reaction.
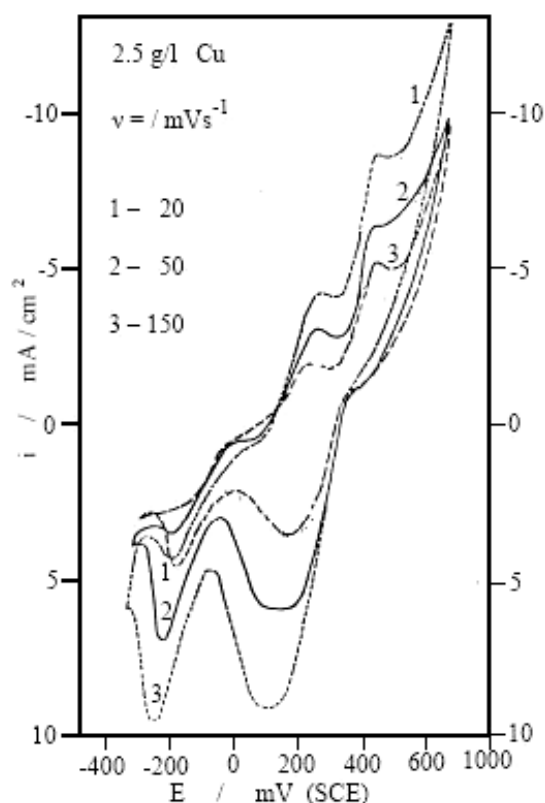

Fig. 7. Influence of the sweeping rate of the potential (v) upon the course of the voltamperogrammes, recorded in copper-containing electrolyte (2.5 g·dm^{-3} Cu in the form of Cu(NO$_3$)$_2$; 40 g·dm^{-3} NH$_4$NO$_3$ and 25% NH$_3$ until pH = 9 is reached) on copper electrode in the range of potentials from E_i = 0.300 V up to E_{sw} = –0.700 V, 1 – v = 20 mV·s^{-1}; 2 – v = 50 mV·s^{-1}; 3 – v = 150 mV·s^{-1}.

The calculations, performed in this way in regard to the second cathodic peak (IIc) and the respective anodic peak (IIa) (Table 2) showed the following. A) The potential in the region of the cathodic peak is slightly shifted anodically with the sweeping rate of the potential. B) The ratio I_p^a/I_p^c > 1 (varying from 1.13 to 2.05) and it is growing up with the square root of the rate $\sqrt{v}$ (Fig. 7); The function of the current $I_p^c/\sqrt{v}$ < 1 (from 0.69 to 0.36) and it is decreasing with the increase of $\sqrt{v}$. These dependencies indicate that this is a CE mechanism, consisting of a reversible electrochemical reaction, preceded by a reversible chemical reaction.

The calculations carried out are an indication that the entire mechanism of deposition of copper from ammonium nitrate electrolyte can be denoted as Electrochemical-Chemical-Electrochemical (EChE) type, i.e. occurring of two consecutive reversible electrochemical reactions (1) and (3) and an intermediate reversible chemical reaction of disproportionation of the copper (2).

CONCLUSIONS

The process of copper deposition from ammonium nitrate electrolyte has been studied at pH = 8.5–9 by the method of cyclic voltamperometry. On the basis of the criteria of this method it has been ascertained that the deposition of copper is proceeding in accordance with an ECE type of mechanism i.e. a mechanism comprising two consecutive reversible electrochemical reactions and an intermediate chemical reaction – disproportionation of the copper.

The experiments carried out form an early stage of the investigation, associated with the process of preparation of alloyed Ag-Cu powders from the above-specified electrolyte.

Table 2. Values of the diagnosis parameters of the cyclic chronovoltamperometry: value (deviation) of the cathodic potential E_p^c, the ratio I_p^a/I_p^c and the function of the current $I_p^a/\sqrt{v}$ on the square root of sweeping of the potential $\sqrt{v}$ for the two cathodic peaks (Ic and IIc) and the respective anodic peaks (Ia and IIa).

UV, (mV·s^{-1})$^{1/2}$	Ic (Ia)			IIc (IIa)		
	E_p^c, mV	I_p^a/I_p^c	I_p^c/ UV	E_p^c, mV	I_p^a/I_p^c	I_p^c/ UV
4.47	–220	1.32	0.43	–465	1.13	0.69
7.07	–270	1.21	0.46	–440	1.64	0.52
12.25	–289	1.07	0.44	–435	2.05	0.36

REFERENCES

1. K.I. Popov, M.G. Pavlovic, in: Electrodeposition of Metal Powders with Controlled Particles Grains Size and Morphology (Modern Aspects of Electrochemistry, vol. 24**)**, B. E. Conway, J. O'M. Bockris, R. E. White, (Eds.), Plenum, New York (1993), pp. 299–391.
2. K. J. Popov, M. G. Pavlovic, J. N. Jovicevic, *Hydrometallurgy*, **23**, 127 (1989).
3. H. M. A. Solimen, H. H. Abdel-Rahman, *J. Braz. Chem. Soc.*, **17**, 705 (2006).
4. K. J. Popov, N. D. Nikolic, M. G. Pavlovic, *J. Serbian Chem. Soc.*, **74**, 397 (2006).
5. K. J. Popov, M. G. Pavlovic, G. Z. Removic, *J. Appl. Electrochem.*, **2**, 742 (1991).
6. M. Seniquchi, K. Nakahara, K. Omal, H. Shimamara, *JP* 169,051 (Cl B22 F 1/00) 17 Jun 2002.
7. A. Tsurkoka, K. Sayama, E. Kazuhiro, *JP* 2000, 290,701 (Cl C B22 F 1/00) 11 Oct 2000.
8. K. Jgnatova, L. Nikolova, E. Kashchieva, *Bull. Electrochem.*, **14**, 315 (1998).
9. C. Nila, J. Gonzales, *J. Electroanal. Chem.*, **401**, 171 (1996).
10. A. Rames, M. M. Hernandes, J. Gonzales, *J. Electrochem. Soc.*, 149, 2002, p. 390.
11. U. J. Larin, E. B. Khobotova, J. D. Gorobets , V. N. Baumer, V. V. Datschenko, *Electrokhimiya*, **26**, 165 (1990).
12. D. Gryjicic, B. Pesic, *Electrochim. Acta*, **50**, 4426 (2005).
13. A. U. Danilov, E. B. Molodhina, Iu. M. Polukarov, *Russ. J. Electrochem.*, **36**, 987 (2000).
14. A. Milchev, T. Zapryanova, *Electrochim. Acta*, **1**, 2926 (2006).
15. D. Stoychev, St. Rashkov, *Compt. Rend. Acad. Bulg. Sci.*, **26**, 243 (1973); *ibid.*, **32**, 1515 (1979); *ibid.*, **50**, 71 (1997).
16. D. Stoychev, St. Rashkov, *Bulg. Chem. Commun.*, **9**, 618; 633; 653 (1976); *ibid.*, **18**, 157 (1985); *ibid.*, **35**, 65 (2003).
17. D. Stoychev, St. Rashkov, *Surf. Technol.*, **7**, 155; 427; 433 (1978); *ibid.*, **10**, 209 (1980).
18. D. Stoychev, I. Tomov, I. Vitanova, *J. Appl. Electrochem.*, **15**, 878 (1985); *ibid.*, **22**, 978 (1992).
19. D. Stoychev, *Trans. Inst. Met. Finishing (England)*, **76** (26); 73 (1998).
20. A. Radisic, G. J. Lany, P. M. Hoffman, P. C. Searson, *J. Electrochem. Soc.*, **148**, 41 (2000).
21. G. Oskam, P. M. Veresken, P. C. Learcon, *J. Electrochem. Soc.*, **146**, 1436 (1999).
22. M. S. Zakharov, O. V. Devyatkova, O. U. Zakharova, *JVUZ Khimiya i Khim. Tekhnol* , **47**, 44 (2004).
23. P. Borthen, J. B. Hwang, H. H. Strechblow, D. M. Koev, *J. Phys. Chem.*, **104,** 5078 (2000).
24. A. J. Bard, L. R. Faulkner, Electrochemical Methods. Fundamentals and Applications, J. Wiley & Sons, New York, 1980, p. 213.
25. Z. Galus, Teoretical Bases of the Electrochemical Analysis, Mir, Moscow, 1974, p. 421 (in Russian).
26. E. R. Brown, R. F. Large, in: Cyclic Voltametry, A Weisberger (Ed.), Wiley Interscience, 1994, Part II A.
27. A. M. Suhotina (Ed.), Handbook in Electrochemistry, Khimia, Leningrad, 1981, p. 133 (in Russian).
28. A. P. Tomilov (Ed.), Industrial Electrochemistry, Khimia, Moscow, 1984, p. 420 (in Russian).

ИЗСЛЕДВАНЕ НА ПРОЦЕСИТЕ И МЕХАНИЗМА НА ЕЛЕКТРООТЛАГАНЕ НА МЕД ОТ АМОНИЕВОНИТРАТЕН ЕЛЕКТРОЛИТ С МЕТОДА НА ЦИКЛИЧНАТА ВОЛТАМПЕРОМЕТРИЯ

Л. Петков*, К. Игнатова

Химико-технологичен и металургичен университет, бул. „Климент Охридски" № 8, 1756 София

В статията са докладвани резултатите от прилагането на метода на цикличната волтамперометрия за изследване на процесите и механизма на отлагане на мед от амониевонитратен електролит. Изследвано е влиянието на началния потенциал, на скоростта на разгъване на потенциала, както и на природата на катодния материал (мед и сребро) върху хода на волтамперограмите. Установено беше, че отлагането на мед върху меден електрод протича по двустадиен механизъм, като чрез редукция на купроамнячните йони. Чрез прилагане на диагностичните критерии на метода беше потвърдено, че механизмът съответствува на ECE, тоест два последователни обратими електрохимични стадия (купри-/купроамонячни комплекси и купроамонячни комплекси/елементарна мед), с междинен химичен стадий на диспропорциониране на медта. Върху сребърен електрод само механизмът на анодния процес е относително същия. Установеното различие в механизма на отлагане на мед е много важно за съвместното отлагане на мед и сребро и получаване на сплавно Ag-Cu покритие, като се има предвид че среброто е по-електроположителният метал в системата.

Получените резултати са важна част от по-обширно изследване, свързано с получаване на сплавен финодисперсен Ag-Cu прах в условията на стационерен и импулсен потенциостатичен режим.