Study of the influence of nitrite anions on the electrode processes in ammonium electrolyte for Ag-Cu deposition

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By means of the cyclic voltammetry (CV) the effect of nitrite anions (in the form of $NaNO_2$) on the kinetics of separate and of codeposition of Ag and Cu is examined. The effect of the electrode substrate and the proportion of the basic components of the solution on the deposition kinetics and the powder formation of Ag-Cu alloys is also established. It is found that the one step process of silver deposition in the absence of nitrite anions is fully reversible. In presence of nitrite anions in the solution, the stage of reduction of the silver-ammonium complexes is preceded by reversible chemical reaction of $AgNO_2$ formation. The copper in nitrite ions absence and presence is deposited by two-stage mechanism – incomplete reduction of the cupri-ammonium ions to cupro-ammonium ions and the main process of electrodeposition of cupri-ammonium ions to elementary copper. As a whole the presence of NO_2^- ions and the decrease of the Ag^+/Cu^{2+} - ratio in the electrolyte impedes the Ag and Cu electrodeposition and results in production of more fine dispersion Ag–Cu alloy powders.

Key words: electrodeposition of alloys, alloy metal powders, cyclic voltammetry

INTRODUCTION

The alloyed Ag–Cu powders find application as components most of all in solder creams in the electronics [1] and in electro-conductive pastes in many areas of the electrical engineering [2, 3].

The electrolysis is a method which allows direct preparation of alloyed metal powders of high purity and dispersibility, controlled phase and component composition [4–6]. The application of non-stationary (impulse) current modes [7, 8], the use of complex electrolytes and the introduction of special additives [6, 8], affecting the crystal growth are becoming more and more frequently applied means in order to meet the high requirements for achievement of maximum dispersibility and morphological homogeneity of the powders.

The thorough analysis of the publications has shown that the ammonium electrolyte may be successfully applied for deposition of finely dispersed Ag–Cu powder [9]. It is well known that these electrolytes are stable during continued operation and permit easy removal of the powder coating from the cathode [9]. In most of the other complex electrolytes for Ag–Cu deposition [10, 11] the silver forms difficult to dissolve compounds, and the electrolytes on their base are unstable.

The ammonium electrolytes are also of theoretical interest for examination of the copper reduction mechanism (the oxidation, respectively) [12–16]. A previous publication of ours is related to the study of this phenomenon in amino-nitrate electrolyte [17]. There is no reference data about the NO_2^- effect on the kinetics and mechanism of Ag and Cu deposition as well as on the structure of Ag–Cu powders. Based on the arguments, pointed out, the composition of the electrolyte, in which we have carried out the present investigations, was chosen.

The method of cyclic voltammetry with its simple qualitative and quantitative criteria [18] is particularly preferred for examination of the alloy deposition. Thus, in the chosen electrolyte composition, the kinetics of separate and co-deposition of Ag and Cu on electrodes of copper and silver is examined as well as the Ag–Cu powder formation.

2. EXPERIMENTAL

The electrolyte in which the studies are carried out has the following composition: Ag – from 2.5 to 7.5 g dm^{-3} in the form of $AgNO_3$; Cu – from 2.5 to 7.5 g dm^{-3} in the form of $Cu(NO_3)_2$; 20–40 g dm^{-3} NH_4NO_3; 0-15 g.dm^{-3} $NaNO_2$ and 25% NH_3 up to pH=9÷9.5. Due to the high solubility of the salts, the preparation of the solution does not give special

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problems. On addition of ammonium, initially at pH 7÷8, the solution becomes cloudy but reaching pH values of 8.5-9 makes the solution transparent, coloured in blue. According to [9, 19] in excess of ammonia in the electrolyte, the silver and copper are in the form of soluble ammonium complexes: $[Ag(NH_3)_2]^+$ and $[Cu(NH_3)_4]^{2+}$, respectively .

The studies are performed in thermostated, three-electrode cell with working electrodes made of copper (99.97%) and silver (96.97%) in the shape of disk with working area of 1 cm^2. The counter electrode is a platinum plate with surface area 30 cm^2, and the working electrode is polarized to different, constant potentials E in reference to a Hg/Hg$_2$Cl$_2$, sat.KCl electrode.

The cyclic voltammograms are recorded by means of potentioscan of "Wenking" type (Germany) in a potential range from 0.600 V ÷ – 1.400 V. The polarization is always from the chosen initial potential in the cathode direction. The rate of potential scanning in the presented voltammograms is varied in the range between 10 and 50 mV.s^{-1}.

The investigation of the alloys morphology is performed by SEM of Oxford Instruments series, JSM-6390 of JEOL.

3. RESULTS AND DISCUSSION

3.1. Voltammograms in Ag electrolyte.

Figure 1(a-c) present the cyclic voltammograms, recorded on silver electrode in an electrolyte which contains 7.5 g dm^{-3}Ag in the presence of a background electrolyte of 40 g dm^{-3} NH$_4$NO$_3$ (Figure 1a) and 15 g dm^{-3} NaNO$_2$ (Figure 1b), as well as in the parallel presence of both background additives of 40 g dm^{-3} NH$_4$NO$_3$ and 15 g dm^{-3} NaNO$_2$ (Figure 1c).

(a)	(b)	(c)
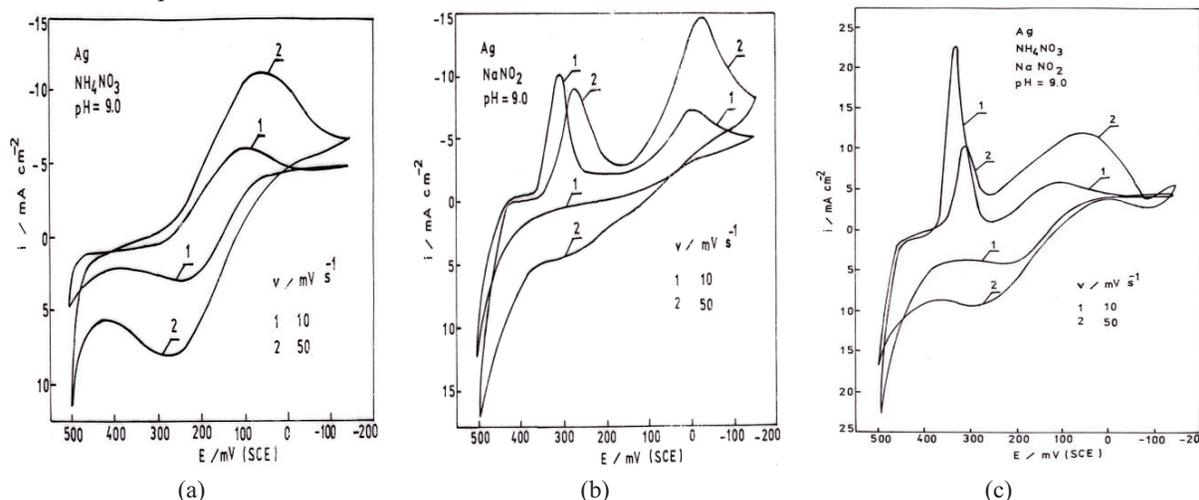
Fig. 1. Voltammograms on Ag electrode in (a): 7,5 g dm^{-3} Ag and 40 g dm^{-3} NH$_4$NO$_3$; (b): 7,5 g dm^{-3} Ag and 15 g dm^{-3} NaNO$_2$ and (c): 7,5 g dm^{-3} Ag; 40 g dm^{-3} NH$_4$NO$_3$ and 15 g dm^{-3} NaNO$_2$,(pH=9,0).

In the presence of NH$_4$NO$_3$ only as a background (Figure1a), observed in the curves are cathode and the corresponding to it anode current maximums that grow proportionally to the rate of potential scanning and the silver ion concentration in the solution.

The current peaks observed are most probably connected with the reduction/oxidation of the forms of silver in accordance with the following reaction:

$$[Ag(NH_3)_2]^+ \; + \; e^- = Ag + 2NH_3 \qquad (1)$$
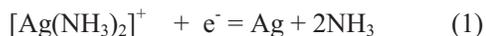
In the presence of NaNO$_2$ as a background, two successive cathode maximums arise, and there is no anode branch (Figure 1b). The detailed examination of the processes in solutions, containing only NaNO$_2$ (data not shown), shows that formation of partially soluble product of AgNO$_2$ is possible at more positive potentials than the steady one, on the electrode surface in accordance with the following reaction:

$$2Ag + NO_3^- + 2H_2O = Ag^+ + AgNO_2 + 2OH^- \;(2)$$

According to the data of Salt Lake Metals, USA [20], the solubility product of AgNO$_2$ is $k_{sp} = 6,0.10^{-4}$, and it is close to that of the AgSO$_4$, ($k_{sp} = 1,4.0.10^{-5}$). Then the first of the maximums in Figure 1b will be resultant from the reaction of AgNO$_2$ reduction to silver:

$$AgNO_2 + 1e^- = Ag + NO_2^- \qquad (3)$$

In the electrolyte, containing 7.5 g dm^{-3}Ag, as well as the background additives: NH$_4$NO$_3$ and NaNO$_2$ (Figure1c), the patterns of relationship that we found, for both background additives separately, become apparent. In this case the electrode surface is characterized by higher activity compared to the electrolyte which contains only sodium nitrite (Figure 1b), and therefore the observed current maximums are higher.

The application of diagnostic criteria of the method of cyclic chronovoltammetry [18] demonstrates that in the electrolyte, containing NaNO$_2$ together with NH$_4$NO$_3$, there is a CE-mechanism observed, i.e. a reversible chemical reaction (Reaction 3) occurs, which precedes the reversible transition of a charge (Reaction 1). It was established that in the electrolyte the potential difference, corresponding with the cathode and the anode currents maxima ΔE^{c-a}, increases with the speed of potential V evolution; the function of the current $(I_c / \sqrt{v})$ decreases with v, and the ratio I_a/I_c increases with the v increase. The same criteria applied for an electrolyte, containing only NH$_4$NO$_3$ as background, testifying for the occurrence of one single reversible electrode reaction, and namely that of the reduction/oxidation of the silver complexes to silver, and vice versa.

3.2. Voltammograms in Cu electrolyte
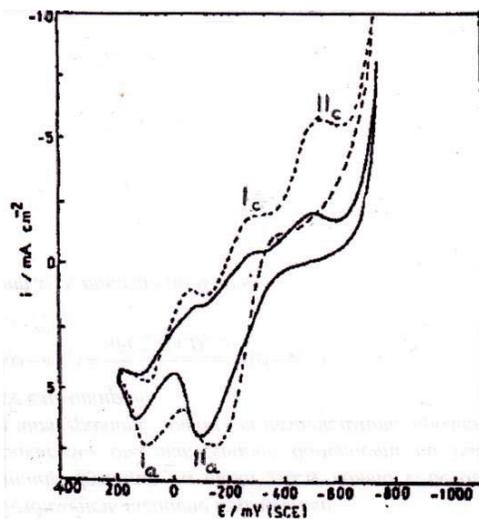
Fig. 2. Voltammograms on Cu electrode in (1): 40 g dm^{-3} NH$_4$NO$_3$ and in (2): 2,5 g dm^{-3} Cu and 40 g dm^{-3} NH$_4$NO$_3$, pH=9.0 (v=30 mV s^{-1}).

We reported in our previous publication [17] on the results of the investigation of the processes of Cu reduction/oxidation in an amino-nitrate electrolyte. It is revealed that in the absence of copper, when the initial potential is much more

positive than the equilibrium, $(E_{eq} = 0.273V)$ two successive cathode peaks (peaks I_c and II_c) are observed, along with the corresponding anode peaks, peak II_a and I_a (Figure 2, curve 1). This data correspond to those, obtained by other authors in ammonia electrolyte [12]. The first cathode peak (I_c), as it follows from the course of the curves, is connected with the reduction of the copper cupri-ammonium ions [Cu(NH$_3$)$_4$]$^{2+}$ to cupro-ammonium ions [Cu(NH$_3$)$_2$]$^+$ in accordance with the reaction below (4):

$$[Cu(NH_3)_4]^{2+} + 1e^- = [Cu(NH_3)_2]^+ + 2NH_3 \quad (4)$$

On reaching the equilibrium concentration, the obtained cupro-ammonium ions [Cu(NH$_3$)$_2$]$^+$ immediately enter in a disproportioning reaction (5):

$$Cu + [Cu(NH_3)_4]^{2+} = 2[Cu(NH_3)_2]^+ + 2NH_3 \quad (5)$$
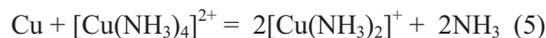
This does not lead to the current peak but rather to its hold on certain level. The second cathode peak (II_c) is connected with the direct reduction of the copper cupri-ammonium complexes to elementary copper according to the reaction:

$$[Cu(NH_3)_4]^{2+} + 2e^- = Cu + 4NH_3 \quad (6)$$
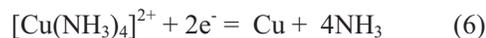
The anode peaks II_a and I_a are connected with a run of reactions, opposite to reactions (6) and (4), respectively. The entire mechanism of copper deposition from amino-nitrate electrolyte is reduced to ECE, running of two successive reversible
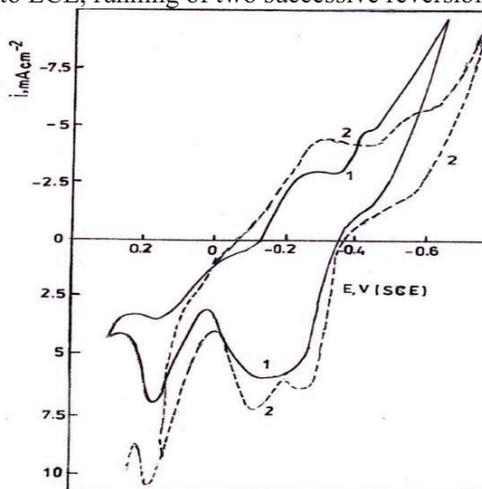
Fig. 3. Voltammograms on Cu electrode in (1): 2,5 g dm^{-3} Cu and 40 g dm^{-3} NH$_4$NO$_3$ and in (2) 2,5 g dm^{-3} Cu, 40 g dm^{-3} NH$_4$NO$_3$ and 15 g dm^{-3} NaNO$_2$, pH=9.0 (v=30 mV s^{-1}).

electrochemical reactions (4) and (6), and of intermediate reversible chemical reaction of copper disproportioning (5) [12, 17].

Fig. 3 presents a comparison between the voltammograms, recorded on copper electrode in 2.5 g dm^{-3} Cu and 40 g dm^{-3} NH$_4$NO$_3$ (Figure 3, curve 1) and in the solution, containing 2.5 g dm^{-3} Cu , 40 g dm^{-3} NH$_4$NO$_3$ and 15 g dm^{-3} NaNO$_2$ (Figure 3, curve 2). The comparison shows that the addition of NaNO$_2$ in the solution results in current increase which corresponds to the incomplete reduction according to reaction (5). Besides, the rate of the useful reaction, that of the cupri-ammonium complexes reduction to copper (6), decreases. An approachment of potentials, corresponding to the two anode peaks, is observed in the anode area. A probable shift of potentials, corresponding to the origination and the respective oxidation of the two complex forms of copper on the anode area, takes place in the presence of NaNO$_2$. Figure 4 presents the voltammograms, recorded in the presence of both background additives and in the presence of copper ions as well, at three different rates of potential scanning. The rate increase of the potential scanning leads to the increase of the current peaks to a different degree, but for all of them the concentration polarization is obviously determinative.

background just of 40 g dm^{-3} NH$_4$NO$_3$. The change of the electrode type leads to current decrease, connected with difficulties in the deposition of metal on an electrode, different in nature. Current decrease is observed on the copper electrode which
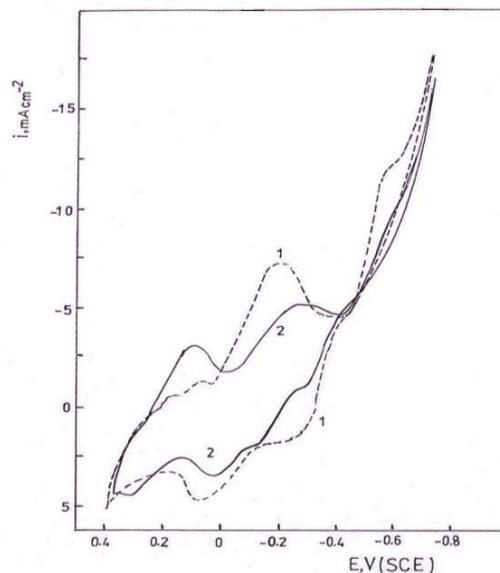
Fig. 5. Voltammograms on Cu electrode (1) and on Ag electrode (2) in 2,5 g dm^{-3} Cu; 2,5 g dm^{-3} Ag and 40 g dm^{-3} NH$_4$NO$_3$, pH=9,0 (v=30 mV s^{-1}).

Fig. 4. Voltammograms on Cu electrode in 2,5 g dm^{-3} Cu, 40 g dm^{-3} NH$_4$NO$_3$ and 15 g dm^{-3} NaNO$_2$, pH=9.0 at scan rates „v": (1) 20 mV s^{-1}; (2) 30 mV s^{-1}; (3) 50 mV s^{-1}.

3.3. Voltammograms in an electrolyte for Cu and Ag co-deposition

The voltammograms, shown in Figure 5, are recorded in an electrolyte for the codeposition of copper and silver on copper electrodes (curve 1), and on silver ones (curve 2) in the presence of a
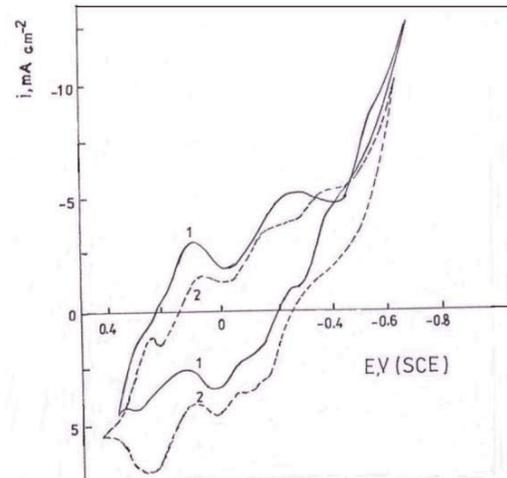
Fig. 6. Voltammograms on Ag electrode in 2,5 g dm^{-3} Cu, 2,5 g dm^{-3} Ag, 40 g dm^{-3} NH$_4$NO$_3$ (1) and in the same electrolyte whit 15 g dm^{-3} NaNO$_2$ (2) ; pH=9.0 (v=30 mV s^{-1}).

is connected with the reduction of the silver ammonium complexes to silver, and on the silver electrode, connected with the reduction of the copper complexes.

The NaNO$_2$ effect on the kinetics of the Ag and Cu codeposition is shown in Figure 6. The

introduction of $NaNO_2$ (Figure 6, curve 2) results in current decrease, connected with the silver and copper reduction – an effect that is established also in the separate deposition of the metals. In the same time, the two-stage mechanism of reduction/oxidation of the copper forms is more clearly visible in the curves, made in the presence of $NaNO_2$ (Figure 6, curve 2) than the curves, made in the absence of $NaNO_2$ (Figure 6, curve 1). Besides, a decrease of the cathode peak and a significant increase (and shift in potentials) of the anode peak, related to the forms of silver, are observed. Obviously, $NaNO_2$ has a significant influence on the joint mechanism of
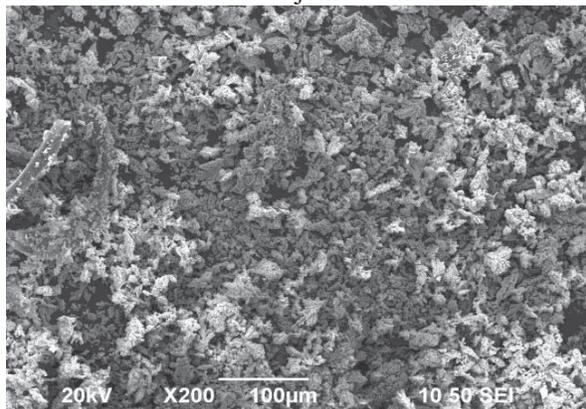
reduction/oxidation of copper and silver, which should reflect on the structure of the Ag–Cu plating, deposited from the electrolyte.

3.4. Morphology of the electrodeposited Ag-Cu powder

Figure 7 (a and b) shows the comparison between the electron micrographs (EM) of the Ag–Cu powder, prepared in the absence (Figure 7a) and in the presence of $NaNO_2$ (Figure 7b) in the electrolyte at the same potential E = – 0,850 V (SCE). The electron micrographs show that in the absence of $NaNO_2$, powders of typically dendrite structure and average size of approximately 50 µm, are formed on the cathode, i.e. the powder
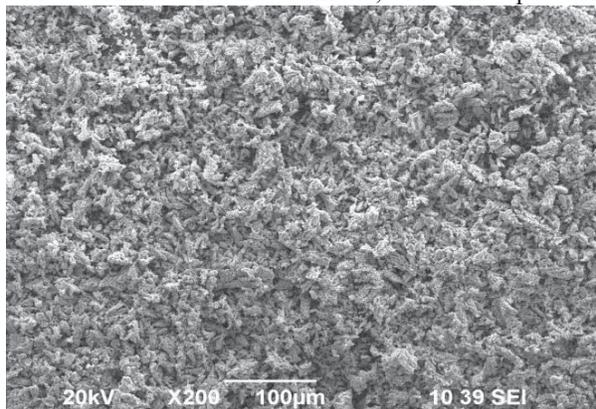
(a)   (b)

Fig. 7. EM of Ag-Cu powder, deposited in 5,0 g dm^{-3} Cu; 5,0 g dm^{-3} Ag; 40 g dm^{-3} NH_4NO_3 , pH=9,0 (A) and in the same composition with 15 g dm^{-3} $NaNO_2$ (B), E = – 0,850 V on Ag-electrode.

dispersity is not sufficiently high (Figure 7a). On the contrary, in the presence of $NaNO_2$, the formed powders are much more finely dispersed (the average size of the particles is approximately 20 µ*m,* more homogeneous in morphological respect (Figure 7b).

4. CONCLUSIONS

It was found that the addition of $NaNO_2$ to the aminonitrate electrolyte for Ag–Cu alloyed powder deposition through its participation in adsorption and chemical processes on the electrode surface changes significantly the mechanisms of both, the separate deposition and the codeposition of the two metals, which results in formation of more finely dispersed Ag–Cu powder.

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ИЗСЛЕДВАНЕ НА ВЛИЯНИЕТО НА НИТРИТНИ АНИОНИ В АМОНЯЧЕН ЕЛЕКТРОЛИТ ЗА ОТЛАГАНЕ НА AG-CU

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(Резюме)

С помощта на метода на цикличната хроноволтамперометрия (CV), е изследвано влиянието на нитритните аниони (под формата на $NaNO_2$) върху кинетиката на самостоятелно и съвместно отлагане на Ag и Cu. Изследван е също и ефекта на природата на електрода (сребро и мед) и съотношението на основните компоненти в разтвора върху кинетиката на отлагане и на прахообразуване на Ag-Cu сплав.

Установено, че в отсъствие на NO_2^- йони, среброто се отлага едностадийно, като процесът е напълно обратим. В присъствие на $NaNO_2$ в разтвора, етапът на редукция на сребърноамонячните комплекси се предшества от обратима химична реакция на образуване на $AgNO_2$, който се редуцира при по-отрицателни потенциали.

Медта в отсъствие и в присъствие на NO_2^- йони се отлага по двустадиен механизъм – непълна редукция на куприамонячните до купроамонячни йони и основният процес на електроотлагане на мед от куприамонячни йони. Като цяло присъствието на NO_2^- и намалението на съотношението Ag^+/Cu^{2+} в електролита подтиска електроотлагането на Ag и Cu и има за резултат формиране на по-финодисперсни Ag-Cu сплавни прахове.