

Influence of the D(+)-glucose on the electrochemical deposition of Ag-Bi alloy from a cyanide electrolyte

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The influence of D(+)-glucose on the electrochemical processes of deposition and dissolution of silver, bismuth and silver-bismuth alloy from a cyanide electrolyte are studied by means of cyclic voltammetry.

The addition of D(+)-glucose has no significant influence on the deposition of silver and relatively weak influence on the deposition of bismuth, but a strong negative effect on the stability of the electrolyte. The excess of free cyanide improves the electrolyte stability, the silver deposition is polarized, and the bismuth becomes a more positive element in the system. The addition of the D(+)-glucose and the increase of its concentration leads to a slight decrease in the bismuth percentage in the coatings.

Dull coatings with high bismuth content can be deposited from the investigated electrolyte. Depending on the free cyanide concentration, the deposition of coatings with bismuth content in the whole range from 0 up to 100 wt. % is possible.

Under certain conditions instabilities in the electrochemical system and resulting potential oscillations could be observed.

Key words: electrodeposition, silver-bismuth alloys, oscillations, D(+)-glucose

INTRODUCTION

Silver-bismuth alloy finds application in electronics, radiotechnics and in the production of coatings, exposed to severe conditions, e.g., friction under high pressure [1,2]. The deposition of this alloy is performed mainly from alkaline electrolytes. The deposition potentials of both metals are relatively close to each other, thus making the alloy deposition not so difficult. The composition of the coatings can be changed depending on the cyanide content in the electrolyte. At a low cyanide concentration, the deposition potential of silver is much more positive than that of bismuth. At a sufficiently high concentration, the deposition potential of silver is strongly shifted in the negative direction, and bismuth becomes the more readily depositing metal. Bismuth deposition is prevailing at the lower current densities [3, 4].

The influence of the electrolyte components and electrolysis conditions on the composition and structure of the alloy have been extensively studied [3- 6]. The properties of single or multi-layered coatings have been described in previous papers [7, 8]. It is known that bismuth and bismuth modified

platinum and palladium electrodes have a strong catalytic effect on the processes of oxidation of various organic substances [9-14]. Particularly appropriate is the use of bismuth in the study of electrochemical oxidation of glucose [12,14,15]. By potentiostatic investigations it has been shown that bismuth can be bonded in complex with glucose or some of its derivatives [12]. Also, well known is the variety of degradation products of glucose in highly alkaline medium [16]. Glucose itself is a desirable additive component in the deposition of some metals and alloys, eg. indium and silver-indium alloys, where its derivatives participate in the formation of complex compounds in alkaline medium, which greatly improves the stability of the electrolytes used [17].

The aim of this work is to study the influence of D(+)-glucose on the electrochemical deposition of Ag-Bi alloys.

EXPERIMENTAL

The composition of the electrolyte for deposition of Ag-Bi alloy coatings is given in Table 1.

Distilled water and *pro analysi* grade reagents were used. The experiments were performed in a

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Table 1. Electrolyte composition

Components	Concentration, mol dm ⁻³
Ag as KAg(CN) ₂	0-0.3
Bi as BiNO ₃	0.1
NaOH	0.64
KNaC ₄ H ₄ ·4H ₂ O	0.42
KCN	0-0.1
D(+)-Glucose	0-0.4

glass cell of 100 cm³ at room temperature (298 K) without stirring of the electrolyte. The working electrode (1 cm²) and the two counter electrodes were made of platinum. A reference electrode Ag/AgCl with $E_{\text{Ag/AgCl}} = -0.197$ V against the hydrogen electrode was used. During the experiments, the reference electrode was placed in a separate cell, filled with KCl solution (3 M). It was connected to the electrolysis cell by a Haber-Luggin capillary through a salt bridge, containing KCl solution of the same concentration. All potentials in the present study are given against this reference electrode.

The cyclic voltammetric investigations were performed by means of a computerized potentiostat/galvanostat, PAR 263A (Princeton Applied Research), using the SoftCorr II software for the electrochemical corrosion studies.

The sweep rate of the potential was varied in the range of 0.005 — 1.000 V s⁻¹. The alloy coatings, *ca.*, 10 μm thick, were deposited in an electrolysis cell of 100 cm³. The silver content in the coatings as well as their thickness were determined using a Fischerscope XRAY XDVM-W apparatus for X-ray fluorescence.

RESULTS AND DISCUSSION

It was shown in a previous paper [4] that the deposition potentials of silver and bismuth are close to each other, thus making the deposition of alloy coatings possible. By means of appropriate complex forming agents, the deposition potential of silver can be strongly shifted in the negative direction, so that bismuth deposition becomes predominant. By changing the electrolyte composition and the conditions of the electrolysis, coatings of any desired composition can be obtained. Figure 1 shows the cyclic voltammetric (CVA) curve in absence of KCN in the alloy deposition electrolyte.

In this case, pure silver coatings are deposited at low current densities. Three cathodic reactions are

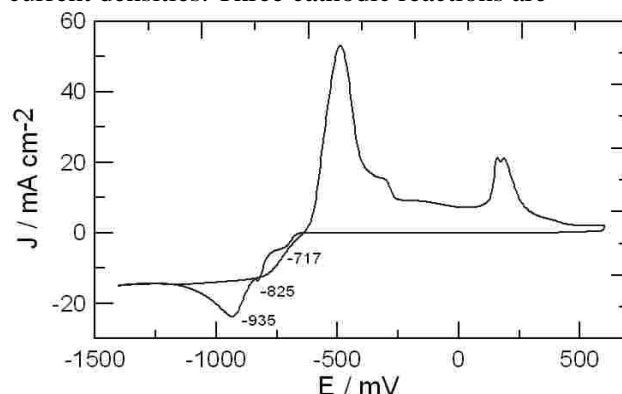


Fig. 1. CVA curves in absence of free cyanide in the electrolyte; $v = 25$ mV s⁻¹, $C_{\text{Ag}} = 0.075$ M; $C_{\text{Bi}} = 0.1$ M; $C_{\text{KCN}} = 0$ M.

observed corresponding to deposition of silver (-717 mV), and deposition of bismuth (-825 mV) and (-935 mV), respectively. The first anodic reaction corresponds to the dissolution of bismuth and the second one to the dissolution of silver. In most cases additional humps to the anodic peaks appear due to incomplete dissolution of the coating and the formation of passive layers, which are dissolved in more positive potentials.

According to the phase diagram of the Ag-Bi alloy [3, 18], the silver crystal lattice could accept up to about 3 wt. % Bi under formation of a solid solution. When the quantity of the co-deposited bismuth exceeds this limit, coatings appear heterogeneous and contain a solid solution of bismuth in silver and pure bismuth [3,5,4]. In many cases, the deposition of phase heterogeneous coatings is related to the onset of instabilities in the electrochemical systems and observation of current or potential oscillations [17, 19, and 20].

Figure 2 presents cathodic current changes with time under potentiostatic conditions at potentials, corresponding to different points of the cyclic voltammetric (CVA) curve. At potentials more positive than -717 mV, the coatings consist of pure silver. With increasing potential in the negative direction, the system reaches the limiting current density for silver, and then the registered currents rapidly increase due to the bismuth co-deposition. On the surface of the electrode the deposition of heterogeneous coating, consisting of darker and lighter areas, is visually observed. The steady state polarization curve, constructed on the basis of the potentiostatic curves, shows different regions, corresponding to different coatings composition (pure silver and Ag-Bi electrolytes). Figure 2 indicates that at potentials, corresponding to the

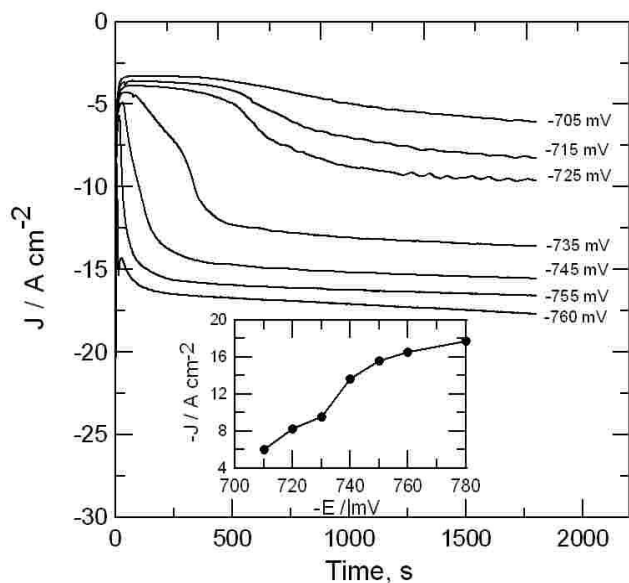


Fig. 2. Cathodic current density during deposition under potentiostatic conditions; (inset stationary polarization curve on the basis of the current transients) $v = 25 \text{ mV s}^{-1}$ $C_{\text{Ag}} = 0.075 \text{ M}$; $C_{\text{Bi}} = 0.1 \text{ M}$; $C_{\text{KCN}} = 0 \text{ M}$

transition from pure silver to alloy deposition (-725 mV), instabilities in the system and oscillations of the cathodic current with time could be observed.

It was shown that, depending on the electrolyte composition and the KCN concentration, the deposition potential of silver could be strongly shifted in the negative direction which results in the preferred bismuth deposition at low current densities [3, 4]. This means that, depending on the concentration of the complex forming agent for silver in the electrolyte, deposition of alloy coatings with bismuth content in a quite broad range is possible. Considering the instability constants for the hydroxide (3.8×10^{-13}) and the mixed hydroxide-tartrate (1×10^{-31}) complexes [21], as well as the high hydroxide content in the electrolyte, it could be presumed that the bismuth deposition process is implemented mainly by the hydroxide and mixed hydroxide-tartrate complexes. The latter are extremely stable, so that the use of other additional complexing agents will not change significantly the deposition potential of bismuth, but may affect the appearance and the structure of the resulting coatings. As such, D(+)-glucose was chosen as substance in these studies.

XPS investigations of bismuth modified platinum electrodes show that Bi species are partially complexed by glucose or its reaction products [12]. Otherwise bismuth electrodes are completely inactive for glucose oxidation, but noble metal catalysts modified with Bi show much better selectivity and activity during the glucose oxidation [12].

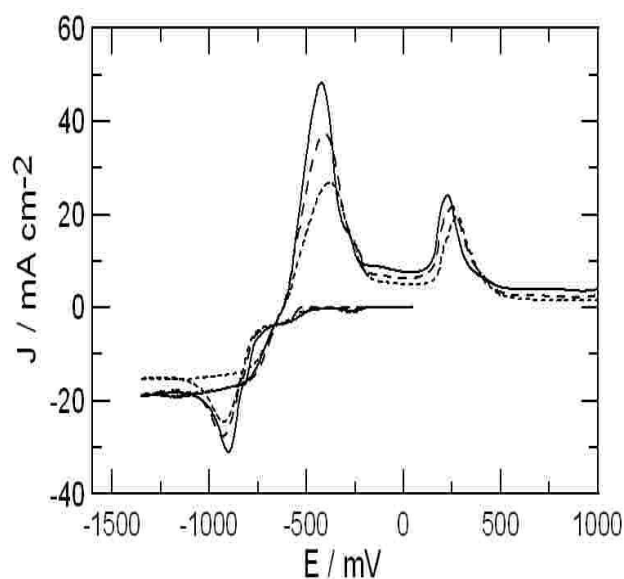


Fig. 3. Effect of $C_{\text{D}(+)\text{-Glucose}}$ in the absence of free cyanide in the electrolyte; $v = 25 \text{ mV s}^{-1}$; $C_{\text{Ag}} = 0.075 \text{ M}$; $C_{\text{Bi}} = 0.1 \text{ M}$; $C_{\text{KCN}} = 0 \text{ M}$; $C_{\text{D}(+)\text{-Glucose}} = \text{---} 0 \text{ M}$; $\text{----} 0.1 \text{ M}$; $\text{.....} 0.3 \text{ M}$

Figure 3 shows the cyclic voltammetric (CVA) curves at different D(+)-glucose concentrations in absence of free cyanide ions in the alloy deposition electrolyte. The increase of the D(+)-glucose concentration leads to a slight polarization and inhibition of the cathodic reactions. A similar conclusion can be made on the basis of the anodic reaction rate at different D(+)-glucose concentrations in the electrolyte. It is obvious that the influence of D(+)-glucose on the deposition of bismuth is not so strong. Probably it is different in a fresh prepared electrolyte compared with a worked electrolyte where the effect of the D(+)-glucose could be stronger. Unfortunately, the addition of D(+)-glucose in absence of free cyanide in the electrolyte lowers its stability and precipitation of silver is observed. The electrolyte becomes dark during one day exploitation. Its stability can be enhanced using appropriate quantities of free KCN as an additional complexing agent for the silver.

The presence of 1 M KCN in the electrolyte leads to additional polarization of the silver deposition with approximately 0.6 V, both in presence or absence of D(+)-glucose. As a result, the silver is deposited at more negative potential than the bismuth, and is dissolved at potentials near to the dissolution potential of the bismuth (Figure 4).

The effect of the D(+)-glucose on the deposition and dissolution processes of silver in the bismuth-free alloy electrolyte in presence of free cyanide is not substantial.

In the silver-free cyanide electrolyte for alloy deposition, the D(+)-glucose exerts some

depolarizing effect and inhibits the cathodic reaction with increasing concentration (Figure 5). This inhi-

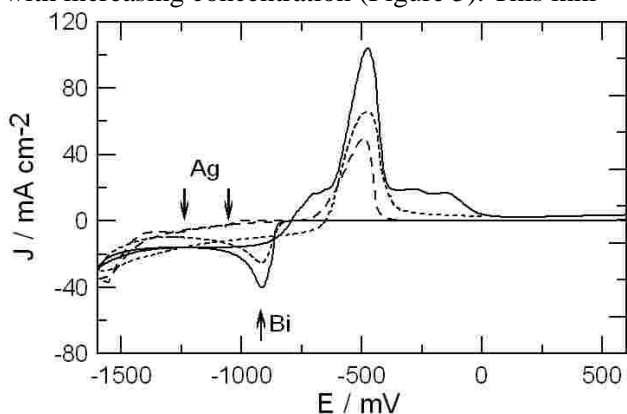


Fig. 4. CVA curves in presence of free cyanide in the electrolyte. $v = 25 \text{ mV s}^{-1}$; $C_{\text{KCN}} = 1 \text{ M}$; $C_{\text{Ag}} = \text{---} 0.075 \text{ M}$ (in absence of Bi); $C_{\text{Bi}} = \text{---} 0.1 \text{ M}$ (in absence of Ag); In the alloy deposition electrolyte $C_{\text{AgBi}} = \text{—} 0.075 / 0.1 \text{ M}$.

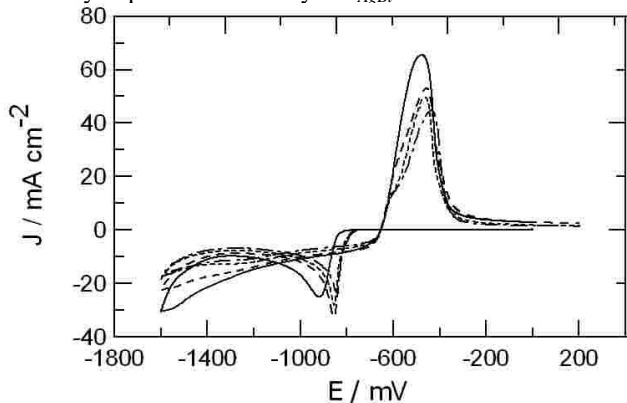


Fig. 5. Influence of $C_{\text{D}(+)\text{-Glucose}}$ on the deposition of bismuth in the presence of free cyanide in the electrolyte; $v = 25 \text{ mV s}^{-1}$; $C_{\text{Ag}} = 0.075 \text{ M}$; $C_{\text{Bi}} = 0.1 \text{ M}$; $C_{\text{KCN}} = 1 \text{ M}$; $C_{\text{D}(+)\text{-Glucose}} = \text{—} 0 \text{ M}$; $\text{---} 0.1 \text{ M}$; $\text{---} 0.2 \text{ M}$; $\text{---} 0.3 \text{ M}$.

bition results in lower deposition rate of bismuth, which is confirmed by comparing the anodic maxima.

In the presence of 1 M KCN, pure bismuth is deposited at low current densities from the alloy deposition electrolyte (Figure 6). The silver content in the coating increases with the increase in the current density. The effect of D(+)-glucose on the deposition of the alloy is similar to its effect on pure bismuth deposition. On the basis of cyclic voltammetric investigations no conclusions could be drawn about the influence of the D(+)-glucose on the deposition of silver from the alloy electrolyte. The first anodic maximum corresponds to the dissolution of silver. Independently of the presence of silver in the electrolyte, the effect of D(+)-glucose on the anodic process is expressed by the dissolution of smaller quantities of electrodeposited bismuth with increased D(+)-glucose concentration and by the disappearance of the more positive peaks, corresponding to the dissolution of passive bismuth

layers. The dissolution of bismuth is easier and more complete with sufficient amounts of D(+)-glucose in

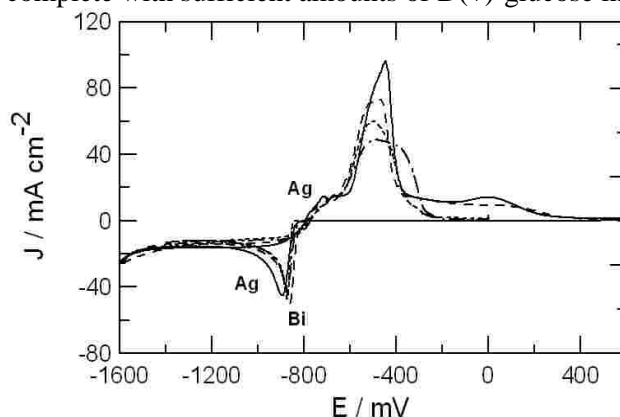


Fig. 6. Influence of $C_{\text{D}(+)\text{-Glucose}}$ on the deposition of alloy in the presence of free cyanide in the electrolyte; $v = 25 \text{ mV s}^{-1}$; $C_{\text{Ag}} = 0.075 \text{ M}$; $C_{\text{Bi}} = 0.1 \text{ M}$; $C_{\text{KCN}} = 1 \text{ M}$; $C_{\text{D}(+)\text{-Glucose}} = \text{—} 0 \text{ M}$; $\text{---} 0.1 \text{ M}$; $\text{---} 0.2 \text{ M}$; $\text{---} 0.3 \text{ M}$

the electrolyte. It can be concluded that glucose and /or its derivatives affect more strongly the electrochemical processes of deposition and dissolution of bismuth than these of the silver. Possibly, the effect of D(+)-glucose on the alloy deposition corresponds to the case of pure bismuth deposition due to the formation of heterogeneous coatings of solid solution of bismuth in silver and pure bismuth [5].

Independently of the presence of D(+)-glucose in absence of free cyanide in the electrolyte, the deposition system is regular according to Brenner [22]. In the presence of free cyanide with increased concentration of D(+)-glucose, the bismuth content of the coatings slightly decrease, as shown in the cyclic voltammetry experiments. Compact coatings can be deposited in the current densities range from 0.2 to 1 A dm^{-2} with bismuth content between 100 and 50 wt. % (Figure 7).

Higher current densities could be applied when higher metal concentrations in the electrolyte are used. Using a silver concentration of 32 g dm^{-3} in the electrolyte, the deposition of coatings with almost constant composition in a broad range of current densities is possible [5].

The observed structures on the heterogeneous coating surface [5] show the possible existence of some instabilities in the electrochemical system, resulting in current (s. Figure 2) or potential oscillations. The oscillations appear under diffusion controlled deposition of the more positive element in simultaneous deposition of a bismuth richer phase. In general, the galvanostatic potential oscillations are not quite regular (Figure 8), which is an indirect indication that the phases form a pattern of spots and chaotic fronts but not periodic waves on the

electrode surface as is the case of the periodic current oscillations during the potentiostatic deposition of Ag-Sb alloy [19, 20].

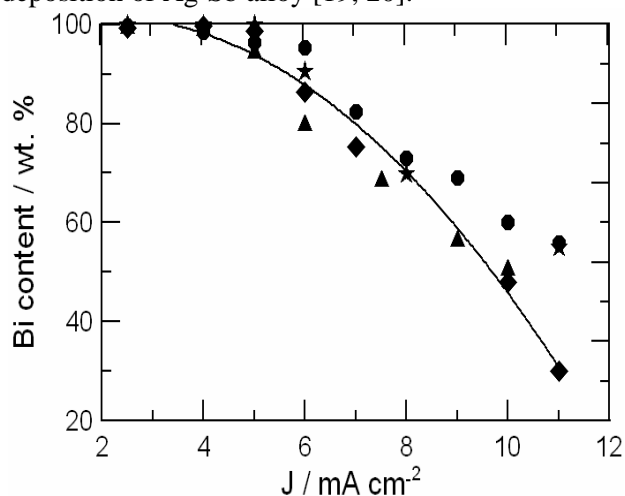


Fig. 7. Influence of the current density and $C_{D(+)-Glucose}$ on the bismuth content in the alloy; $C_{Ag} = 0.075$ M; $C_{Bi} = 0.1$ M; $C_{KCN} = 1$ M; (●) - $C_{D(+)-Glucose} = 0$ M; (★) - $C_{D(+)-Glucose} = 0.025$ M; (◆) - $C_{D(+)-Glucose} = 0.1$ M; (▲) - $C_{D(+)-Glucose} = 0.2$ M.

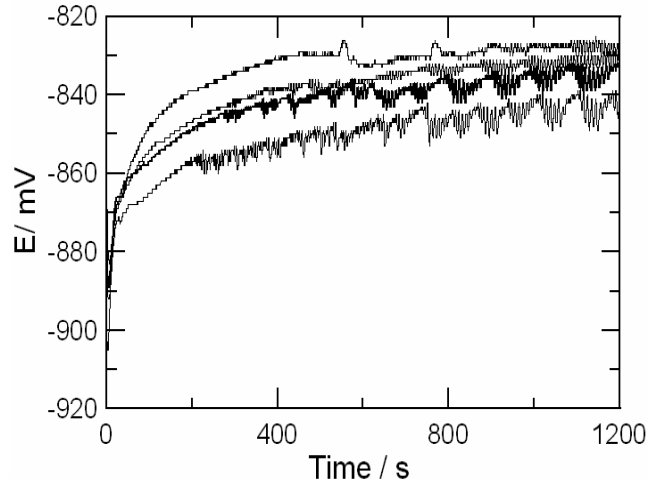


Fig. 8. Potential oscillations during the deposition of the alloy under galvanostatic conditions.; $C_{Ag} = 0.3$ M; $C_{Bi} = 0.1$ M; $C_{KCN} = 1$ M; $C_{D(+)-Glucose} = 0.1$ M

The investigations allow to conclude that the addition of D(+)-glucose to the alkaline electrolyte for deposition of Ag-Bi alloys has no significant influence on the deposition of silver and has relatively weak influence on the deposition of bismuth, with a strong negative effect on the stability of the electrolyte. The excess of free cyanide improves the electrolyte stability, the silver deposition is polarized, a strong depolarization of its dissolution is observed, and the bismuth becomes the more positive element in the system. The addition of the D(+)-glucose and the increase of its concentration leads to a slight decrease in the bismuth percentage in the coatings.

Dull coatings with high bismuth content can be deposited from such an electrolyte. Depending on the free cyanide concentration the deposition of coatings with bismuth content in the whole range from 0 up to 100 wt. % is possible. Under certain conditions instabilities in the electrochemical system and resulting potential oscillations could be observed, which could be of interest for further investigations.

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ВЛИЯНИЕ НА D (+)-ГЛЮКОЗАТА ВЪРХУ ЕЛЕКТРОХИМИЧНОТО ОТЛАГАНЕ НА СРЕБЪРНО-БИСМУТОВИ СПЛАВИ ОТ ЦИАНИДЕН ЕЛЕКТРОЛИТ

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(Резюме)

Изследвано е влиянието на D(+)-глюкозата върху електрохимичното отлагане на сребро, бисмут и сребърно-бисмутова сплав от цианиден електролит с помощта на циклична волтамперометрия.

Добавянето на D(+)-глюкоза няма значимо влияние върху отлагането на среброто. То оказва сравнително слабо влияние върху отлагането на бисмут, но има силно отрицателно въздействие върху стабилността на електролита. Излишъкът на свободен цианид подобрява стабилността на електролита, отлагането на сребро се поляризира, а бисмутът става по-положителният елемент в системата. Добавянето на D(+)-глюкоза и повишаването на концентрацията ѝ води до слабо понижение на концентрацията на бисмут в покритията.

От изследвания електролит се отлагат матови покрития с високо съдържание на бисмут. То зависи от концентрацията на свободния цианид в електролита и може да варира между 0 и 100 тегл. %.

В някои случаи се наблюдават неустойчивости в електрохимичната система водещи до осцилации на катодния потенциал.