ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2016, Vol. 90, No. 5, pp. 1081–1087. © Pleiades Publishing, Ltd., 2016.
Original Russian Text © T.N. Vorobyova, H.M. Maltanova, O.N. Vrublevskaya, 2016, published in Zhurnal Fizicheskoi Khimii, 2016, Vol. 90, No. 5, pp. 800–807.

Formation of Alloys upon the Simultaneous Electrochemical Deposition of Gold and Tin from Ethylene Glycol and Aqueous Electrolytes

T. N. Vorobyova[a,b], H. M. Maltanova[a], and O. N. Vrublevskaya[a]
[a] *Research Institute of Physico-Chemical Problems, Belarusian State University, Minsk, 220030 Belarus*
[b] *Belarusian State University, Minsk, 220030 Belarus*
e-mail: vorobyovatn@gmail.com

Received June 3, 2015

Abstract—An ethylene glycol (EG) solution containing Au(III) and Sn(IV) compounds, and conditions for the electrochemical deposition of Au–Sn alloy based on AuSn and Au_5Sn intermetallics with total tin content of 30–55 at % are proposed. Fundamental difficulties of the deposition of alloys with high tin content, (including eutectic Au–Sn alloy) from aqueous electrolytes are revealed. It is determined via voltammetry that the simultaneous deposition of gold and tin from aqueous and EG electrolytes proceeds with the depolarization effect of both Au(III) and Sn(IV) as a result of the formation of the alloy, the increase in the rate of tin cathodic reduction being more noticeable in case of EG solution. Formation of $SnCl_2EG(H_2O)_2^{2+}$ complex upon the dissolution of $SnCl_4 \cdot 5H_2O$ in glycol, the stability of the composition of tetracyanoaurate ions upon the dissolution of $K[Au(CN)_4]$, and the weakening of intermolecular interactions in EG with small amounts of water were revealed via IR spectroscopy. It is suggested that the depolarization effect is due not only to alloy formation, but also to the formation of $SnCl_2EG(H_2O)_2^{2+}$ cations, their association with $Au(CN)_4^-$ anions, and a change in the mechanism of Au(III) and Sn(IV) reduction.

Keywords: electrochemical deposition, intermetallics, Au–Sn alloy, depolarization, complexation.
DOI: 10.1134/S0036024416050356

INTRODUCTION

Compared to metallurgical and vacuum technologies, the electrochemical deposition of metal alloys is an energy efficient process that allows the saving of metals due to the local deposition of coatings with the required thickness. A disadvantage of the processes for synthesizing alloys from solutions is the complexity of regulating the ratio of metals in the products, their phase composition, and their microstructure. Alloys deposited from solutions often have non-equilibrium phase composition and include phases that are thermodynamically stable only at high temperatures [1, 2].

In this work, we describe the electrochemical synthesis of a binary gold–tin alloy with a definite phase composition. Eutectic Au–Sn alloy is used as solder in assembling of various devices, hermetizing frames of integrated circuits and optoelectronic devices, and connecting conductors based on copper alloys [3, 4]. The eutectic includes Au_5Sn and AuSn crystalline phases at a total tin content of 30 at %. It has a melting point of 278°C and low viscosity in molten state. Au–Sn coatings with compositions close to eutectic have dense fine-grained microstructure without dendrites and whiskers. They can be decorative in appearance, and have good electrical and thermal conductivities and corrosion resistance [5].

It is well known that aqueous electrolytes of three types are used for electrodeposition of Au–Sn alloys: acidic ($pH < 3$) electrolytes containing cyanide complexes of gold(III) and tin(IV) compounds [4, 6], slightly acidic or neutral solutions (pH 3–7) based on tetrachloroaurate(III) ions and tin(II) compounds [7], and alkaline solutions ($pH > 10.5$) based on gold(I) cyanide complex and tin(IV) compounds [8]. The main disadvantage of slightly acidic aqueous solutions is the low reproducibility of the elemental and phase composition of alloys as a result of the instability of electrolytes due to the hydrolysis of Sn(II, IV) compounds, and to the reduction of Au(I, III) by tin(II) compounds present in the solutions or formed as a result of the partial reduction of Sn(IV). In strongly acidic or strongly alkaline solutions, etching of the substrate can occur. In addition, the reduction of metals from aqueous solutions is often accompanied by

Table 1. Dependence of the growth rate (*V*) and the elemental and phase compositions of Au–Sn coatings on electrolyte composition (where *C* is concentration of constituents), temperature (*T*), and current density (*j*).

Electrolyte number, solvent	$C_{Sn(IV)}$, mol/L	$C_{Au(III)}$, mol/L	*T*, °C	*j*, mA/cm^2	*V*, μm/h	Elemental composition, at %	Phase composition
1, EG	1.4	0.05	35	10	2.0	Au–64, Sn–36	No crystalline phases
				5	1.8	Au–69, Sn–31	Au_5Sn, AuSn
			20	5	1.0	Au–59, Sn–41	AuSn, Au_5Sn
2, EG	1.4	0.1	35	10	3.0	Au–55, Sn–45	AuSn
				5	2.4	Au–58, Sn–42	Au_5Sn, AuSn
			20	1	1.0	Au–56, Sn–44	Au_5Sn, AuSn
3, 1 M HCl in water	1.4	0.05	20	5	4.3	Au–92, Sn–8	Au_5Sn, AuSn, amorph. Au
4, 1 M HCl in water	1.4	0.1	35	5	4.9	Au–94, Sn–6	Au_5Sn, Au
				1	0.9	Au–100	Au

cathodic hydrogen evolution, which degrades the quality of the coatings.

The electrodeposition of Au–Sn alloy from nonaqueous electrolytes would therefore seem to be promising. Among the possible solvents suitable for use in electroplating, EG is perhaps the most promising. It is a polar liquid and has rather low volatility up to 50–70°C, but its electrical conductivity is less than that of water (1.07×10^{-6} S cm^{-1} vs. 4.5×10^{-3} S cm^{-1}) [9]. The solubility of salts of metals in EG is quite high, and dissolution is often accompanied by the formation of complex compounds $Me(EG)_n^{2+}$ with Co(II), Ni(II), Cu(II), Mg(II), Ca(II), and Sr(II) [10–12]. A disadvantage of EG is its high viscosity compared to water: $\eta_{EG} = 19.830$ mPa s, $\eta_{H_2O} = 1.002$ mPa s [9].

When we began the present studies, glycol-based electrolytes for tin and nickel deposition were well known, as were tin-plating solutions based on glycol/choline chloride mixtures [13–15]. This information was the basis for developing ethylene- and propylene-glycol solutions that allow the electrochemical deposition of Au–Sn alloy. In [16–19], we demonstrated the possibility of deposition of Au–Sn coatings with tin contents of up to 60–70 at. % and determined specific conditions for the deposition of a eutectic alloy based on Au_5Sn and AuSn intermetallics with total tin content of 30 at %. We were unable to establish the factors that determine the efficient co-deposition of tin with gold, or the nature of the processes that ensure the formation of crystalline intermetallic phases when using EG as a solvent. The aim of this work was to establish the reasons for the differences between elemental and phase compositions of Au–Sn alloy that forms during electrochemical deposition from EG and aqueous electrolytes, and to determine the conditions necessary for the electrocrystallization of gold–tin intermetallics.

EXPERIMENTAL

The simultaneous electrochemical deposition of gold and tin was conducted using aqueous and EG electrolytes containing $K[Au(CN)_4]$ and $SnCl_4 \cdot 5H_2O$ (Table 1). The choice of cyanide ions as ligands for Au(III) was due to the requirement for the high stability of the complex compound to ensure the stability of electrolytes and the maximal shift of the electrode potential of gold towards negative values. In accordance with recommendations presented in earlier studies on the electrochemical deposition of tin from glycol solutions [20], Sn(IV) was introduced in the form of tin(IV) chloride pentahydrate, which is stable and readily soluble in glycols. Tin and gold were present in the chosen compounds in a higher oxidation state, which was necessary to prevent redox processes in the bulk of solutions, and to reduce the gold content in the alloy, since Au(III) is much harder to reduce than Au(I). The Sn(IV) concentration in our solutions was more than an order of magnitude higher than that of Au(III), as was required for the convergence of the electrode potentials of the metals and to increase the proportion of tin in the alloy. The ratio of $K[Au(CN)_4]$ to $SnCl_4 \cdot 5H_2O$ concentrations was varied within a wide range, however, Table 1 shows only the compositions of those solutions that basically ensure formation of the eutectic. The total water content in solutions 1 and 2 was about 6 wt %, including the crystallization water of $SnCl_4 \cdot 5H_2O$ and the water absorbed from the air. To study the role of water, the electrochemical deposition of tin, gold, and Au–Sn alloy was conducted using electrolytes dried in a desiccator over freshly calcined calcium chloride, and from aqueous electrolytes in which an aqueous solution of HCl with a concentration of 1 mol/L was used as a solvent to prevent the hydrolysis of Sn(IV) compounds (Table 1, solutions 3 and 4).

The coatings were deposited under stirring with a magnetic stirrer in the temperature range of 20–35°C. Current density was varied in the range of 1–10 mA/cm^2, since coatings of unsatisfactory quality and poor adhesion to the substrate formed at higher current densities, and colloidal gold formed in aqueous solutions. Platinum foil (99.99%) was used as anode, and copper foil (99.9%) was the cathode. The growth rate of the coatings was estimated by weight, taking into account the gold : tin ratio.

The elemental composition of the coatings was determined via energy dispersive X-ray microanalysis (EDX) using a Rontec attachment on a LEO 1420 scanning electron microscope. The phase composition of the alloys was determined via X-ray diffraction analysis (XRD) on a DRON 3 unit. The IR spectra of solutions were recorded on an AVATAR 330 spectrometer (Thermo Nicolet) in the region of 400–4000 cm^{-1} with an accuracy of 1 cm^{-1}. The samples were prepared for analysis by applying thin layers of the investigated solution onto steel plates.

Voltammetric curves (VAM) were recorded in the potentiodynamic mode using an Autolab PGSTAT 302N potentiostat/galvanostat at a scan rate of 20 mV s^{-1}. To consider the ohmic drop in the volume of EG solution, recording was done in the *iR*-error compensation mode using currentless measurements of the electrode potential. No compensation was required in aqueous electrolytes. A three-electrode cell with a platinum auxiliary electrode, a silver chloride reference electrode, and a working copper electrode (foil with an area of 1 cm^2) was used. For VAM study we used EG and aqueous solutions 2 and 4 (Table 1), along with solutions of similar composition, but including either $K[Au(CN)_4]$ (2-Au, 4-Au) or $SnCl_4 \cdot 5H_2O$ (2-Sn, 4-Sn) only, and with background electrolytes containing 6 wt % of water and 0.1–0.8 mol/L of sodium chloride in EG (solution 5) or in HCl solution with a concentration of 1 mol/L (solution 6).

RESULTS AND DISCUSSION

It was found that virtually no gold, tin, or Au–Sn alloy was deposited from dried EG solutions. When 6 wt % of water was added to EG containing 0.1 mol/L of $K[Au(CN)_4]$, only traces of gold were observed on the surface of the cathode, and the slow deposition of very fine (less than 0.05 μm thick) gold films from an aqueous potassium tetracyanoaurate solution with a concentration of 0.1 mol/L occurred. From an EG $SnCl_4 \cdot 5H_2O$ solution containing ~6 wt % of water, rather dense and relatively fine-grained coatings formed with virtually no dendrites, distinguishing them from the ones obtained from an aqueous electrolyte with similar composition in [20]. When current density (*j*) was increased from 5 to 10 mA/cm^2, the growth rate of tin coatings from EG solution rose from 2.5 to 4.5 μm/h.

In case of simultaneous presence of $K[Au(CN)_4]$ and $SnCl_4 \cdot 5H_2O$ in EG, the deposition of dense light grayish-yellowish Au–Sn coatings occurred only from solutions containing no less than 6 wt % of water when $j = 1–10$ mA/cm^2. The growth rate of the Au–Sn coatings rose in the range of 1–6 μm/h when *j* was increased from 1 to 10 mA/cm^2, the concentration of Sn(IV) in the solution was decreased from 2.8 to 1.4 mol/L, the temperature of the solutions was raised from 20 to 35°C, and water was added into them (Table 1). Note that all of the changes in the composition of electrolytes and their temperature lead to a drop in their viscosity.

The tin content in the Au–Sn coatings depended strongly on the composition of the electrolytes and conditions of deposition, and could vary from 0 to 55 at %. The maximum tin content was achieved when deposition was conducted using EG electrolytes at room temperature and when current density was raised to ~20 mA/cm^2. The factors that determine the phase composition of Au–Sn alloys were established. Thus, crystalline phases of gold–tin intermetallics were deposited from EG solutions. AuSn formed most often; Au_5Sn appeared more rarely (Table 1). When the current density was high and/or the content of Sn(IV) was raised to 2.8 mol/L, crystalline $AuSn_2$ and $AuSn_4$ could form in the solution [16–18]. The formation of crystalline tin and gold phases is not typical for glycol solutions. When $j = 10$ mA/cm^2 and the tin content in coatings is higher than 35 at. %, X-ray amorphous phases sometimes form. Alloys deposited from aqueous solutions 3 and 4 often include crystalline gold in addition to AuSn and Au_5Sn. Regardless of the composition of the electrolyte, the electrocrystallization of AuSn and Au_5Sn phases is observed only when the tin content in the alloy lies in the range of 10–44 at %. This is a necessary but not sufficient condition for the formation of intermetallics corresponding to the eutectic composition.

During the simultaneous deposition of tin and gold from aqueous electrolyte 4 at $j = 10$ mA/cm^2 and room temperature, Au–Sn coatings grow at a maximum rate of 10 μm/h and have elemental and phase compositions quite close to eutectic, but with a somewhat lower tin content (22 at %). However, the electrolyte is not stable under these conditions.

The IR spectra of $K[Au(CN)_4]$ and $SnCl_4 \cdot 5H_2O$ EG solutions were studied to explain the nature of the strong influence the solvents (EG and water) on the chemical and phase composition of deposited Au–Sn coatings (Fig. 1). Analysis of the IR spectra of $K[Au(CN)_4]$ solutions in EG showed that the complexation of Au(III) with glycol does not occur, since there was no shift in the bands of C–OH and CH_2 bond vibrations in the region of 1460–1080 cm^{-1} that

Table 2. Potentials of appearance of cathode current ($E_{\text{begin.reduct}}$, mV) at copper electrode in EG and aqueous solutions, and cathode current density at potentials of −500 and −550 mV (j_{500} and j_{550}, mA/cm^2)

Solution	2-Sn	2-Au	2-Au–Sn	5	4-Sn	4-Au	4-Au–Sn	6
$E_{\text{begin.reduct}}$	−430	−475	−430	−1185	−470	−500	−430	−740
j_{500}	2.0	0.05	8.5	0	5.0	0.1	8.5	0
j_{550}	5.2	0.1	17.0	0	35.0	1.0	57.0	0

The deposition of coatings with good quality and composition closest to the eutectic composition occurs in this region of potentials and currents.

are characteristic of EG. The wavenumbers of the C–H bond vibrations (2975–2860 cm^{-1}) in the EG solution were also unchanged. In all cases, Δν did not exceed the measurement error (±1 cm^{-1}). The strong line at 2200–2000 cm^{-1} characteristic of the valence vibrations of terminal CN groups was observed in the spectrum of potassium tetracyanoaurate in EG [21]. The frequencies of the bands of valence vibrations of OH bonds in the investigated solution shifted lower by 26–40 cm^{-1}, due possibly to attenuation of the association of EG molecules in the presence of tetracyanoaurate anions. The wave numbers of the peak corresponding to the HOH vibrations (1680–1630 cm^{-1}) of water molecules changed only slightly (by 1–4 cm^{-1}), allowing us to assess the invariability of their chemical environment [22]. Me–C bond vibrations in Au–CN were observed in the region of 480–420 cm^{-1} [21].

Considerable changes in the solvent spectra occurred upon the dissolution of $SnCl_4 \cdot 5H_2O$ in EG (Fig. 1). We described these changes in [20], and concluded that complex compounds with $SnCl_2EG(H_2O)_2^{2+}$ composition formed with the participation of both hydroxyl groups of the EG molecules. At the same time, a weakening of the intermolecular interaction in the solvent environment was observed. This weakening apparently helps to intensify mass transfer in the solvent, and the positive charge of $SnCl_2EG(H_2O)_2^{2+}$ complex ions contributes to their diffusion to the cathode and their discharge.

In the IR spectra of EG solutions that simultaneously contain Au(III) and Sn(IV) compounds, peak shifts and new bonds not characteristic of EG generally repeat the changes in spectra observed upon the dissolution of individual $SnCl_4 \cdot 5H_2O$ and $K[Au(CN)_4]$. These data indicate the presence of $SnCl_2EG(H_2O)_2^{2+}$ complex cations and $[Au(CN)_4]^-$ anions in the EG solutions, along with the weakening of intermolecular interaction in EG in the presence of small amounts of water.

The cathodic branches of the polarization curves reflecting the electrochemical behavior of copper electrodes in aqueous or EG solutions of $K[Au(CN)_4]$ and/or $SnCl_4$, and in background solutions 5 and 6, were recorded to study the patterns of the separate and

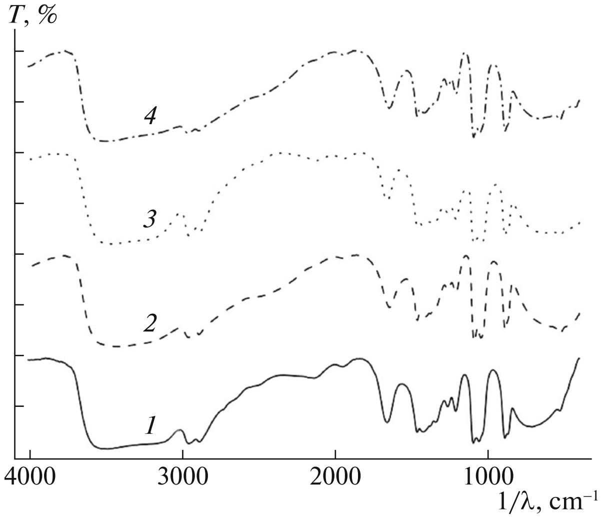

Fig. 1. IR spectra: (*1*) EG, (*2*) 1.4 M $SnCl_4 \cdot 5H_2O$ solution in EG, (*3*) 0.1 M $K[Au(CN)_4]$ solution in EG, and (*4*) $SnCl_4 \cdot 5H_2O$ and $K[Au(CN)_4]$ solutions in EG with concentrations of 1.4 and 0.1 mol/L, respectively.

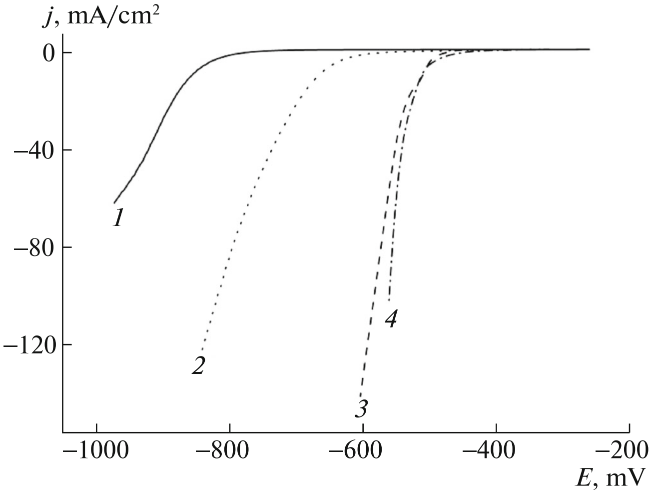

Fig. 2. Cathodic branches of voltammograms reflecting the behavior of copper electrode in aqueous solutions of (*2*) $K[Au(CN)_4]$ and (*3*) $SnCl_4 \cdot 5H_2O$; (*4*) both these salts and (*1*) in aqueous background solution 6.

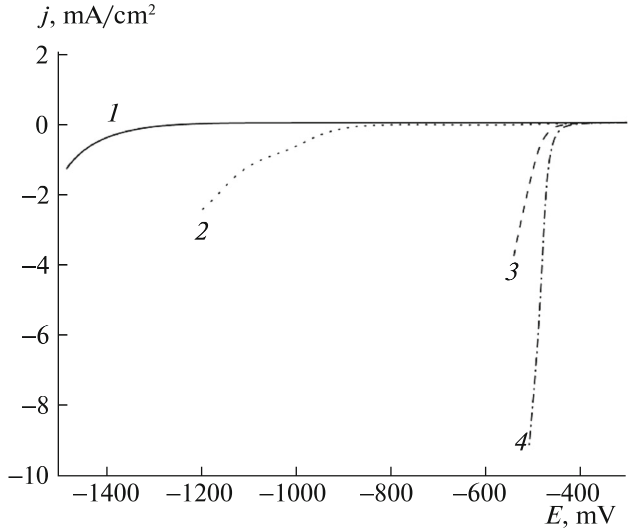

Fig. 3. Cathodic branches of voltammograms reflecting the behavior of copper electrode in EG solutions of (*2*) K[Au(CN)$_4$] and (*3*) SnCl$_4$ · 5H$_2$O; (*4*) both these salts and (*1*) in EG background solution 5.

simultaneous reduction of tin(IV) and gold(III) (Figs. 2 and 3; Table 2).

The cathode current corresponding to the evolution of hydrogen in aqueous background solution 6 was observed at potentials more negative than −740 mV (Fig. 2, curve *1*), and in background EG solution 5 at −1185 mV (Fig. 2, curve *1*). With acidified potassium tetracyanoaurate aqueous solution 4-Au, the cathodic current of gold(III) reduction on copper electrode appeared at a potential of −500 mV. Up to −650 mV, the current grew only slightly (to 2 mA/cm^2 only) (Fig. 2, curve *2*). The path of the cathodic branch of polarization curve is similar to the one described in [23, 24], according to which the region of low currents corresponds to the reduction of Au(III) to Au(I) with the partial cleavage of cyanide ions from [Au(CN)$_4$]$^-$ ions slightly distorted in the electric field. Poorly soluble AuCN is adsorbed on the cathode. As a result of electron transfer, a discharge of Au$^+$, the desorption of CN$^-$ ions, the diffusion of Au atoms on the surface of the cathode, and their incorporation into the crystal lattice of gold nuclei occur. With a further cathodic potential sweep, the rate of cathodic reduction increases sharply, and the current reaches 24 mA/cm^2 at −700 mV when hydrogen has not yet evolved. The authors of [23, 25] attributed the current in this potential range to the reduction of Au^{3+} ions formed during the dissociation of complex tetracyanoaurate ions distorted in a strong electric field, to Au^0. The reduction of Au(III) is described by the scheme

$$\begin{aligned}
&\text{(a) } \mathrm{Au(CN)_{4\,ads}^{-} + 2e \rightarrow AuCN_{ads} + 3CN^{-}};\\
&\text{(b) } \mathrm{AuCN_{ads} + e \rightarrow Au_{ads} + CN^{-}};\\
&\text{(c) } \mathrm{Au(CN)_{4ads}^{-} \leftrightarrow Au_{ads}^{3+} + 4CN^{-}};\\
&\text{(d) } \mathrm{Au_{ads}^{3+} + 3e \rightarrow Au_{ads}}.
\end{aligned} \qquad (1)$$

The cathodic current corresponding to tin(IV) reduction from aqueous solution 4-Sn appears at a potential of −475 mV and increases with further cathodic potential shift, reaching 10 mA/cm^2 at −500 mV, where individual gold(III) is not reduced (Fig. 2, curve *3*). At −550 mV, the current of Sn(IV) reduction is 35 times stronger than that of Au(III) (Table 2). The polarization curve has an inflection in the region of −(515–530) mV; according to [26], at more anodic potentials the reduction of Sn(IV) to Sn(II) occurs, at more negative potentials Sn(II) is reduced to Sn(0) according to the scheme

$$\begin{aligned}
&\text{(a) } \mathrm{SnCl_6^{2-} + 2e \rightarrow SnCl_4^{2-} + 2Cl^{-}};\\
&\text{(b) } \mathrm{SnCl_4^{2-} + 2e \rightarrow Sn + 4Cl^{-}}.
\end{aligned} \qquad (2)$$

The substantially higher Sn(IV) reduction current density as compared to Au(III) reduction is due not only to the higher (an order of magnitude) concentration of tin(IV) compounds, but also to the multistage mechanism of the reduction of Au(III) cyanide complex.

The cathodic current corresponding to the simultaneous reduction of Au(III) and Sn(IV) from aqueous electrolyte 4-Au–Sn is observed from −430 mV, i.e., earlier than for the reduction of individual Sn(IV) or Au(III) (Fig. 2, curve *4*). At potentials of −500 and −550 mV, the cathodic current of the simultaneous reduction of Au(III) and Sn(IV) is 8.5 and 57 mA/cm^2, respectively, exceeding the reduction currents of both Sn(IV) and Au(III). The data testify to the effect of the depolarization of the cathodic reduction of both metals, which is especially pronounced in the case of Au(III) reduction. Hydrogen evolution was not observed in the range of currents and potentials where dense films of tin, gold, or their alloys are deposited. This is consistent with the available data on high overpotential of hydrogen evolution on tin [26] and gold [23–25].

The appreciable effect of the depolarization of Sn(IV) cathodic reduction could be due to the process of alloy formation, but this explanation is not enough when very strong depolarization of Au(III) reduction is observed. In the range of potentials up to −530 mV, tin(II)—a product of stage 2a of Sn(IV) reduction probably reduces Au(III) from tetracyanoaurate ions adsorbed on the surface of the cathode, according to the scheme

$$\begin{aligned}
&\text{(a) } \mathrm{SnCl_6^{2-} + 2e \rightarrow SnCl_4^{2-} + 2Cl^{-}};\\
&\text{(b) } \mathrm{SnCl_4^{2-} + 2AuCN_{ads}}
\end{aligned}$$

$$+ 2Cl^- \rightarrow SnCl_6^{2-} + 2Au + 2CN^-; \quad (3)$$

or partial

$$(c)\ 3SnCl_4^{2-} + 2Au(CN)_4^-$$

$$+ 6Cl^- \rightarrow 3SnCl_6^{2-} + 2Au + 8CN^-.$$

As a result, the concentration of gold in the deposited alloy is greatly exceeds the one we might expect based on the proximity of potentials of the onset of the cathodic reduction of Sn(IV) and Au(III). Experimental results show that at high current densities, colloidal gold forms in the bulk of the electrolyte as a result of reaction 3c.

When 6 wt % of water is introduced in a 0.1 M solution of potassium tetracyanoaurate in EG (solution 2-Au), a very weak cathodic current is observed for the copper electrode at potentials more negative than −475 mV (Fig. 3, curve *2*; Table 2). When the potential is shifted to −1000 mV, the current of gold(III) reduction is only 0.8 mA/cm^2. These data confirm that gold coatings cannot be deposited from a 0.1 M solution of potassium tetracyanoaurate in EG. The cathodic reduction of tin(IV) from $SnCl_4 \cdot 5H_2O$ solution in EG (solution 2-Sn) begins at a potential of −430 mV, which is less negative than that of Au(III) reduction from tetracyanoaurate ions. The current of tin(IV) reduction grows rapidly when the potential shifts to the cathodic region and reaches ~5 mA/cm^2 at −550 mV, which roughly corresponds to the current density for the deposition of tin coatings from EG electrolyte. In EG solution 2-Au–Sn containing $K[Au(CN)_4]$ and $SnCl_4 \cdot 5H_2O$, the cathodic current appears at −430 mV, as in the case of $SnCl_4 \cdot 5H_2O$; however, the slope of the polarization curve is much steeper than in the EG-based electrolyte containing Sn(IV) only (Table 2). The simultaneous reduction of gold and tin is confirmed by the change in the appearance of the electrode: the copper is covered with a golden-gray film of the alloy. The evolution of hydrogen is not observed during the reduction of Au(III) and/or Sn(IV). These results prove the depolarization effect of the cathodic reduction of both gold(III) and tin(IV). The difference between the slopes of the curves indicates that the depolarization effect of Sn(IV) reduction is much more noticeable when using EG solutions, as compared to aqueous solutions.

One of the reasons for this effect is the formation of an alloy based on intermetallics of gold and tin. This has been confirmed by XRD data and is especially characteristic of EG solutions. Another reason for the efficiency of the simultaneous cathodic reduction of Au(III) and Sn(IV) from EG solutions would appear to be interactions between the Au(III) and Sn(IV) complex compounds dissolved in the EG and these compounds with the solvent. As we indicated in [20], the formation of $SnCl_2EG(H_2O)_2^{2+}$ complex cations weakens the intermolecular interaction in EG. Along with the presence of a positive charge, this promotes their diffusion to the cathode in an electric field. The value of the potential of the onset of Sn(IV) cathodic reduction (−430 mV) indicates that according to the ability to dissociate in EG, this complex compound does not differ greatly from $SnCl_6^{2-}$ chloride complexes in water (−470 mV). It is possible that Sn(IV) cathodic reduction in EG also proceeds in two stages similar to 2a and 2b, with both chloride ions eventually splitting off from Sn(II), a product of partial reduction.

The positive charge of Sn(IV) complex ions in EG promotes their Coulomb interaction with negatively charged tetracyanoaurate ions, while such interaction is not possible in aqueous solutions where Au(III) and Sn(IV) are included in the composition of anions. We can assume that as a result of the formation of $SnCl_2EG(H_2O)_2^{2+}$–$Au(CN)_4^-$ associates in EG, the transportation of Au(III) and Sn(IV) to the Helmholtz layer in an electric field becomes more efficient, as do the distortion and decay of complex $Au(CN)_4^-$ anions and $SnCl_2EG(H_2O)_2^{2+}$ cations in the layer. It is possible that in EG-based electrolyte, stages 1a and 1b do not occur in the electroreduction of Au(III), and stages 1c and 1d become possible even at low electric field intensities because the delivery to the cathode and release of Au^{3+} ions are ensured.

The virtually simultaneous discharge of Au(III) and Sn(IV) that occurs on the adsorption site of an associate containing them evidently promotes the electrocrystallisation of intermetallics. In the EG-based electrolyte Sn(II), a product of the first reduction stage of Sn(IV), is not consumed in concurrent reduction of AuCN; along with the depolarization effect of the cathodic reduction of Sn(IV) and the convergence of electrode potentials of gold and tin due to complexation, this ensures a high proportion of tin in the resulting alloy.

Of particular note is our explanation of the role of small amounts of water in EG electrolytes, since the deposition of tin, gold (in trace amounts), and Au–Sn alloy occurs only when water is present. Experimental data from IR spectroscopy and measurements of viscosity indicate that water weakens the intermolecular interactions in EG, thereby promoting the diffusion of ions in the solution. In the presence of water $SnCl_2EG(H_2O)_2^{2+}$ complex playing a crucial role in the electrodeposition of the alloy is formed.

CONCLUSIONS

1. The modes of operation and composition of ethylene glycol solution ($SnCl_4 \cdot 5H_2O$ and $K[Au(CN)_4]$ at a molar ratio of 14 : 1, 6 wt % of water) that ensure electrochemical deposition of Au–Sn alloy based on AuSn and Au_5Sn intermetallics with tin contents cor-

responding to the eutectic composition (30 at %) or raised to 55 at % were determined. It was shown that it is extremely difficult to obtain alloys of eutectic composition from aqueous solutions, due to the dominance of gold content in the products of electrochemical deposition. It was found that tin content in an alloy grows with increase of current density, at lower temperatures, and with decrease of water concentration down to 6 wt %, while gold, tin, and their alloys are not deposited from completely anhydrous EG solutions.

2. It was shown via voltammetry that the simultaneous reduction of gold and tin from aqueous and EG electrolytes occurs with depolarization effect of the reduction of both Au(III) and Sn(IV), due largely to the formation of Au–Sn alloy, the depolarization effect of cathodic deposition of tin being more pronounced in the EG electrolyte.

3. Analysis of cathodic branches of voltammograms showed that the reduction of individual gold(III) and tin(IV) proceeds in two stages. Upon the simultaneous reduction of Au(III) and Sn(IV) from aqueous electrolyte, Sn(II)—a product of the first stage of Sn(IV) reduction—is consumed in the reduction of Au(I) in AuCN adsorbed on the cathode, which is a product of the first stage of Au(III) reduction. As a result, the content of gold in the deposit exceeds the estimations, and the phases of gold or gold-rich Au_5Sn intermetallic are formed. We assume that upon simultaneous reduction of gold and tin from EG electrolyte, there is no spontaneous consumption of Sn(II) for Au(I) reduction.

4. It was determined via IR spectroscopy that the formation of complex compounds of the $SnCl_2EG(H_2O)_2^{2+}$ type occurs upon the dissolution of $SnCl_4 \cdot 5H_2O$ in EG. As a result, the intermolecular interactions in the solvent environment are weakened, and $Au(CN)_4^-$ ions do not interact with EG. The rate of deposition of tin and Au–Sn alloy coatings (up to 2 μm/h, which is quite high for nonaqueous electrolytes), and the effect of pronounced depolarization of Sn(IV) and Au(III) electroreduction from EG electrolyte, are explained by the increased rate of diffusion and the discharge of $SnCl_2EG(H_2O)_2^{2+}$ cations, along with their associates with $Au(CN)_4^-$ anions.

5. It was found that a small amount of water is needed in EG electrolyte (5–7 wt %) to weaken the intermolecular interaction in the glycol and thus facilitate the transport of Au(III) and Sn(IV) ions in an electric field, and to ensure the formation of $SnCl_2EG(H_2O)_2^{2+}$ complex cations.

REFERENCES

1. V. V. Povetkin, I. M. Kovenskii, and Yu. I. Ustinovshchikov, *The Structure and Properties of the Electrolytic Alloys* (Nauka, Moscow, 1992) [in Russian].
2. Yu. D. Gamburg, *Electrochemical Crystallization of Metals and Alloys* (NFKh, RAN, Yanus-K, Moscow, 1997) [in Russian].
3. B. Djurfos and D. G. Ivey, Mater. Sci. Eng. B **90**, 309 (2002).
4. B. Bozzini, A. Fanigliulo, G. Giovannelli, et al., J. Appl. Electrochem. **33**, 747 (2003).
5. G. Ghosh, J. Mater. Res. **23**, 1398 (2008).
6. B. Bozzii, P. Cavallotti, A. Fanigliulo, et al., J. Solid State Electrochem. **8**, 147 (2003).
7. J. Doesburg and D. Ivey, Mater. Sci. Eng. B **78**, 44 (2000).
8. B. Bozzini, G. Giovannelli, S. Natali, et al., J. Appl. Electrochem. **32**, 165 (2002).
9. A. Weissberg, E. Proskauer, J. Riddick, and E. Toops, *Organic Solvents* (Intersci., New York, 1955; Mir, Moscow, 1958).
10. O. Yu. Sytnik, A. P. Krasnoperova, Yu. N. Surov, et al., Visn. Khark. Univ., Khim. **13** (36), 56 (2005).
11. A. Miyake, Bull. Chem. Soc. Jpn. **32**, 1381 (1959).
12. D. Knetsh and W. L. Groeneveld, Inorg. Chim. Acta **7**, 81 (1973).
13. C. D. Gu, Y. J. Mai, J. P. Zhou, et al., J. Power Sources **214**, 200 (2012).
14. O. N. Vrublevskaya and T. N. Vorobyova, Izv. NAN Belarusi, Ser. Khim. Nauk, No. **2**, 64 (2010).
15. *Electrodeposition from Ionic Liquids,* Ed. by F. Endres, D. MacFarlane, and A. Abbott (Wiley-VCH, Weinheim, 2008).
16. T. N. Vorobyova and O. N. Vrublevskaya, Surf. Coat. Technol. **204**, 1314 (2010).
17. H. M. Maltanava, O. N. Vrublevskaya, and T. N. Vorobyova, Metal. Finish. **111** (6), 28 (2013).
18. H. M. Maltanova, O. N. Vrublevskaya, and T. N. Vorobyova, Mir Gal'vaniki, No. 1 (26), 40 (2014).
19. H. M. Maltanova, T. N. Vorobyova, E. S. Veretennikova, and O. N. Vrublevskaya, Izv. NAN Belarusi, Ser. Khim. Nauk, No. 3, 10 (2014).
20. H. M. Maltanava, T. N. Vorobyova, and O. N. Vrublevskaya, Surf. Coat. Technol. **254**, 388 (2014).
21. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part A. Theory and Applications in Inorganic Chemistry,* 6th ed. (Wiley-VCH, New York, 2009).
22. J. B. Zhang, P. Y. Zhang, K. Ma, et al., Sci. China. Ser. B: Chem. **5**, 420 (2008).
23. B. Bossini, B. Busson, G. P. de Gaudenzi, et al., J. Electroanal. Chem. **602**, 61 (2007).
24. F. Huerta, C. Mele, B. Bossini, and E. Morallon, J. Electroanal. Chem. **569**, 53 (2004).
25. P. Wilkinson, Gold Bull. **19** (3), 75 (1986).
26. Y. Zhang, in *Modern Electroplating,* Ed. by M. Schlesinger and M. Panovic, 5th ed. (Wiley, New York, 2010), p. 139.

Translated by V. Kudrinskaya