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Assessment of phase composition of electrolytic deposits by stripping voltammetry

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Abstract

This paper describes the method of assessing the composition of the intermetallic compounds in nanoscale electrolytic deposits. The formula was developed for calculating the deflection potential in the case of selective electrooxidation electronegative component of the alloy composition. The processes of electro binary electrolytic precipitation in mercury-rhodium chloride electrolyte by anodic stripping voltammetry were studied. It was established that an electrolytic precipitate contains rhodium, mercury and rhodium IC with mercury composition Hg₃Rh.

Keywords: stripping voltammetry, intermetallic compound, rhodium, mercury, indium, binary precipitate

Introduction

A matter of special interest in the stripping voltammetry (SV) method is the phase composition of electrolytic deposits with co-electrodeposition of two or more elements as the infusion of the foreign metals into the electrolytic deposit often changes the polarization characteristics of the electro-oxidation of the individual components.¹

The behaviour of the binary systems in the framework of the stripping voltammetry method is studied by most researchers only with the reference to the practical analysis carried out by this method. On the one hand, the approaches allowing for the exclusion of the mutual influence of the sample components are developed, and on the other hand the introduction of an additional element (typically Hg or Bi) in system is used for the increasing the sensitivity in determining some elements (modified electrodes). One of the ways of application of the binary systems is the possibility to indirectly evaluate the electrochemically inactive element in the presence of the second element, which forms intermetallic compounds together with the first element (IC)². Meanwhile, the research of the phase composition of the electrolytic deposit often fades into insignificance. The methods of analysis of the phase

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composition of the resulting binary electrolytic deposits are used extremely rarely, such as X-ray diffraction or electron diffraction, apparently due to the large experimental difficulties associated with the small amounts of the substance formed on the electrode.

Thus, the aim of this work was to develop the assessment methodology for the phase composition of the nanoscale binary electrolytic deposits by the method of stripping voltammetry and to evaluate the phase composition of binary electrolytic deposits of mercury-rhodium in the chloride electrolytes.

2. Experiment

All the research works were performed using the voltammetric analyzers TA-4 (SPE “Tomanalyt”, Tomsk) and a personal computer. The quartz glasses with the volume of 20 cm³ were used as the electrolysis cells. The working electrode was an impregnated polyethylene graphite electrode (GE), the comparative electrode and a secondary electrode were silver chloride electrodes (s.c.e.) filled with a saturated solution of KCl.

The electrodeposition of the binary electrolytic deposits was realized from the solutions containing ions of mercury (II) and rhodium (III). Rhodium was used as a chloride complex $[\text{RhCl}_6]^{3-}$. The electrochemical cleaning of the electrode surface was carried out in the background electrolyte during a minute at a potential of 1.0 V. The surface of the electrode was renewed after each measurement. During the electrolysis the solution was mixed automatically by the vibration of the working electrode, which is provided by the used analyzers. All the research works were performed with the use of the reagents with the qualifications not lower than “chemically pure” under normal conditions.

3. Results and discussion

The research experiments were carried out in a solution of 1M HCl. The typical current-voltage curves of the electrooxidation of the binary electrolytic deposit mercury-rhodium from the surface of the graphite electrode are shown in Fig. 1. The peak at a potential of + 0.06 V corresponds to the process of electrooxidation of the mercury deposited on the surface of the GE (mercury phase peak). The peak at a potential of 0.325 V depends on the concentration of rhodium ion (III) in the solution and on the concentration of the mercury ions (II). The further increase of the concentration of rhodium ions (III) (curve 2) leads to the decrease of the peak at a potential of 0.06 V and the increase of additional anodic peak at a potential of 0.325 V. Moreover, the current of the additional anodic peak (curves 1 and 2) is directly proportional to the concentration of rhodium ions (III) in the solution. The potential of the additional anodic peak is not changed when changing the rhodium content in the electrolytic deposit. This shows the consistency of the phase structure, from which the electrooxidation of rhodium occurs.

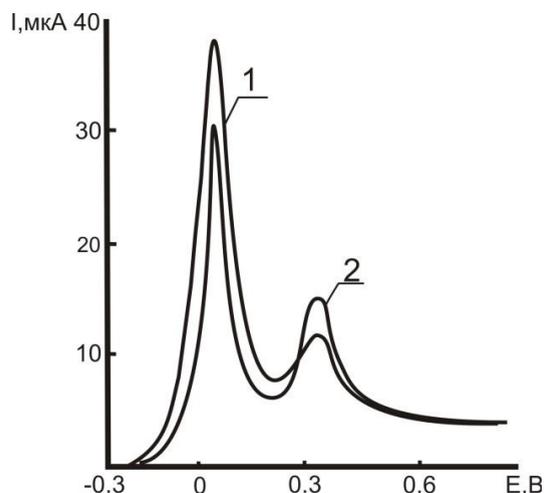


Fig. 1. The current-voltage curves of the electrooxidation of the binary electrolytic deposit mercury-rhodium from the graphite electrode surface. The experimental conditions: background 1 M HCl, $E_c = -1.0$ V, $\tau_c = 100$ s, $v = 80$ mV/s, $C_{\text{Hg}^{2+}} = 100$ mg/L; 1) $C_{\text{Rh}^{3+}} = 0.1$ mg/L; 2) $C_{\text{Rh}^{3+}} = 0.2$ mg/L.

As it is seen from Fig.1, when the rhodium content increases in the electrolytic deposit the anodic peak of mercury lowers. Thus, on the voltage-current curve an additional anodic peak appears at a potential of 0.32 V, the current which is dependent both on the concentration of mercury ions (II) and the concentration of rhodium ions (III) in the solution.

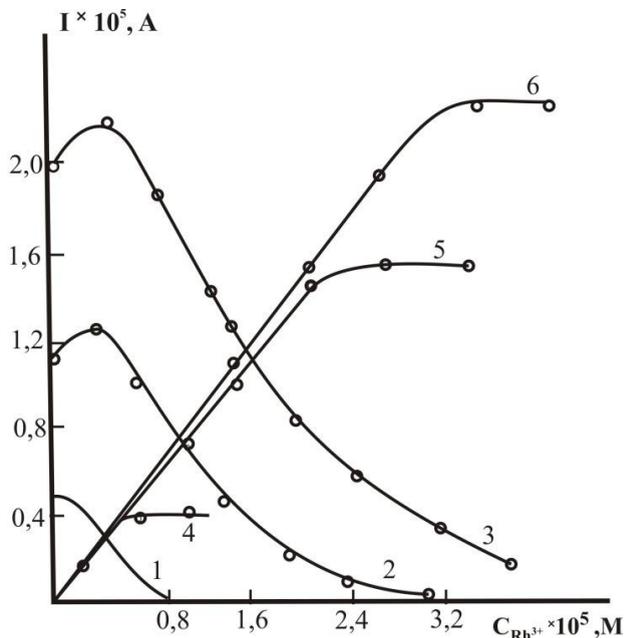


Fig. 2. Graphs of dependence of mercury anodic peak and additional anodic peak currents on the ion concentration of rhodium (III) in a solution; background: HCl - 1 mol/L; $E_e = -0.6$ V; $\tau_e = 120$ s; $C_{Hg^{2+}}$, mol/L: (1,4) - $1.6 \cdot 10^{-5}$; (2,5) - $4.8 \cdot 10^{-5}$; (3,6) - $8 \cdot 10^{-5}$

Fig. 2 shows the dependency graphs for the current of the mercury anodic peak and the current of an additional anodic peak of the ion concentration of rhodium (III) in the solution. As it is seen from Fig. 2 the current of the additional anodic peak increases in proportion to the content of the ions of rhodium (III) in the solution with the constant content of mercury ions (II) in the solution up to a certain limit. The current of the mercury anodic peak decreases at the increase of the content of rhodium in the solution and accordingly in the electrolytic deposit. With the increase of the content of the mercury ions in the solution and, of the mercury in the electrolytic deposit the further increase of the additional peak current is possible proportionally to the content of the ions of rhodium (III) in the solution.

Our research experiments revealed that at a constant amount of mercury and a variable amount of rhodium in the deposit the total amount of electricity consumed in the oxidation of mercury from the alloys with rhodium remains constant. This is possible if an additional anodic peak at a potential of 0.325 V, is caused by the selective electrooxidation of mercury from the intermetallic compound (IC) with rhodium.

According to the phase diagram³ mercury and rhodium form three ICs: RhHg₅, RhHg_{4.53}, RhHg₂, which correspond to the rhodium mole fractions 0.17, 0.18, 0.33. The selective electrooxidation of the compositionally different ICs should form anodic peaks at different potentials.

We found that the offset of the anodic peak potential of the mercury in the formation of the solid solution on the electrode or IC can be calculated by the relation:

$$\Delta E_{pa} = E_{pa} - E_{pa}^{mix} = \frac{RT}{zF} \ln X_i - \frac{(1-X_i)^2}{zF} \varepsilon_{mix} \quad (1)$$

where

E_{pa} – anodic peak potential of electronegative component in a pure phase;
 E_{pa}^{mix} – anodic peak potential at its selective electrooxidation from an alloy;
 ε_{mix} – integral heat of components mixing in the formation of a solid solution or IC;
 X_i – is a mole fraction of electronegative component in the alloy.

As is known, during the alloy forming the heats of mixing are equivalent to forming a covalent bond between the metals. Calculating the binding energy of the two metals in the cell structure can be realized by using Pauling correlation equation⁴:

$$\varepsilon_{mix} = \frac{1}{2}(\varepsilon_{A-A} + \varepsilon_{B-B}) + 100(\chi_A - \chi_B)^2 - 6,5(\chi_A - \chi_B)^4 \quad (2)$$

where ε_{A-A} , ε_{B-B} – is the dissociation energy of the metal - metal bindings;
 χ_A , χ_B – the electronegativity of the alloy components.

There are no published data on the binding energy of the Rh-Rh, so we calculated this binding energy from the heat of rhodium sublimation⁵.

Thus, in order to calculate the mixing energy the dissociation energy of metal-metal bindings were used: $\varepsilon_{Hg-Hg} = 35.081$ kJ/mol; $\varepsilon_{Rh-Rh} = 99.802$ kJ/mol and the electronegativity of the metals: $\chi_{Rh} = 2.28$; $\chi_{Hg} = 2$. The heat of mixing of the components of rhodium or mercury calculated from these data is 67.449 kJ/mol.

Knowing the heat of mixing it is possible to calculate the value of the offsets of peak potentials of the selective electrooxidation of mercury IC with rhodium relative to the peak potential of mercury electrooxidation from the GE surface, and then the anodic peak potentials of mercury IC with rhodium by the formula:

$$E_{pa}^{mix} = E_{pa} - \Delta E_{pa} \quad (3)$$

The results of the calculation of the anodic peak potential of the selective electrooxidation of mercury IC with rhodium are shown in Table 1.

Table 1. Comparison of the calculated and experimentally determined values of the peak potentials of the selective electrooxidation of mercury IC with rhodium

Anodic peak potential of Hg, V ($E_{pa(Hg)} = 0.06$ V)	Phase structure		
	RhHg ₅ $X_{Rh}=0.17$	RhHg _{4,53} $X_{Rh}=0.18$	RhHg ₂ $X_{Rh}=0.33$
$\Delta E_{pa, calc.}$	-0.264	-0.284	-0.171
$E_{pa, calc.}$	0.324	0.344	0.231
$E_{pa, exp.}$	0.325	-	-

By calculating the peak bias potentials of the mercury electrooxidation it is possible to estimate the potential of the additional anode peak and on this basis to determine what phase structure corresponds to the peak of mercury selective electrooxidation of IC with rhodium. Data in the Table 1. show that the observed anodic peak at a potential of 0.32 V corresponds to the selective electrooxidation of mercury IC with rhodium of the composition RhHg₅. The current value of this additional anodic peak can be used for analytical purposes to determine the ions Rh (III) by the method of anodic stripping voltammetry.

4. Conclusion

1. The technique was developed for estimating the phase composition of the nanoscale structures of the electrolytic deposits forming the solid solutions using the method of stripping voltammetry.
2. The electrooxidation processes of the binary electrolytic deposit of mercury-rhodium were examined. It was shown in the current-voltage curve that apart from the electrooxidation mercury peak at more positive potentials an additional peak is observed, the current of which is dependent both on the concentration of mercury ions (II) and the concentration of rhodium ions (III) in the solution.
3. It was found that the observed additional anodic peak is caused by the selective electrooxidation of mercury IC with rhodium. An assessment of the phase compositions of IC mercury with rhodium was made in accordance with the offset of the peak potential of the mercury electrooxidation.
4. It was demonstrated that an additional anodic peak on the current-voltage curve of the electrooxidation of mercury-rhodium deposit was caused by the selective electrooxidation of mercury IC Hg₅Rh.

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