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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.

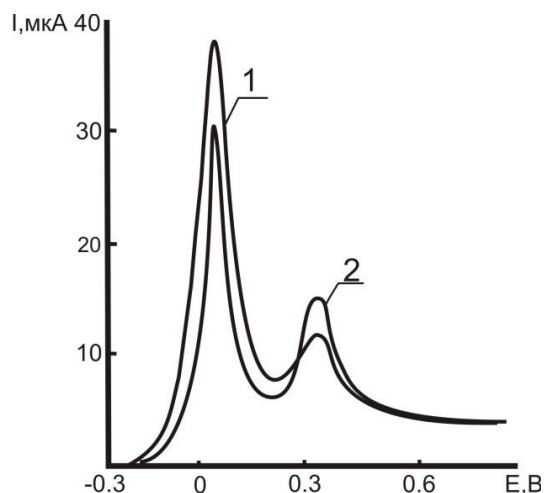


Fig. 1. The current-voltage curves of the electrooxidation of the binary electrolytic deposit mercury-rhodium from the graphite electrode surface. The experimental conditions: background 1 M HCl, $E_c = -1.0$ V, $\tau_c = 100$ s, $v = 80$ mV/s, $C_{\text{Hg}^{2+}} = 100$ mg/L; 1) $C_{\text{Rh}^{3+}}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

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