UDC 541.138+541.135.3

S.A. Kochetova (1), research worker, c.ch.s.
A.V. Savchuk (1), junior research worker
N.F. Kutshevskay (2), professor, d.t.s.
I.M. Astrelin (3), professor, d.t.s.
V.V. Malyshev (1,2), professor, d.t.s.

ELECTROCHEMICAL BEHAVIOR AND ELECTRODEPOSITION NANO-STRUCTURED RHODIUM FROM LOW TEMPERATURE CARBAMIDE- AND ACETAMIDECOMPRISING FUSIONS

(1) V.I.Vernadsky institute of general and inorganic chemistry NASU, Kyiv, Ukraine,
(2) Open international university of man development «Ukraine», Kyiv, Ukraine,
(3) National university «KPI», Kyiv, Ukraine

Nanoflakes and materials on their basis show unique electric, chemical, magnetic, optical, catalytic and other properties and that is considerable pay attention is these researches [1-3]. In connection with the wide area of the use of nanocomposite materials in modern technologies the methods of their synthesis are developed [4]. Therefore an important value is had methods of electrochemical renewal for complex connections of metals in low temperature fusions.

This work is devoted to the study of electrochemical synthesis for ion complex connections of rhodium in ion-organic fusions on the basis of carbamide and acetamide to careful research of their properties and structure with the use of spectroscopy methods and realization of the cathode deposition of nanocoverages of rhodium on different metallic bases.

For determination of electrochemical properties for solvent and research of electrochemical behavior of rhodium in carbamide- and acetamidecomprising fusions the method of cyclic voltammeter are applied. As an anode used a plate from the investigated metal, platinum feed bar served as an auxiliary electrode, as an electrode of comparison - the semielement of Ag/Ag^+. Researches executed in a temperature interval 80-130 °C at the atmosphere of argon.

Study of the state of metal ions in fusions after electrochemical dissolution, structure and composition of complex connections carried out with the use of spectroscopy methods: method of electronic spectroscopy of absorption in the process of electrolysis (Specord UV/VIS), infrared Spectroscopy of hardenings after an electrolysis fusions (Specord M-80) and gas chromatography (LCHR-80).

Composition of the got metallic fallouts was determined by a roentgen phase method (DRON-3) and structure of sediment - by the methods of electronic translucent microscopy (JEOL-100) and raster electronic microscopy (REM-101).

Anodic dissolution of rhodium was carried out in fusion of individual carbamide and eutectic fusion of carbamide-NH_4Cl (16,8 %) at a temperature 130 °C. In an individual molten carbamide dissolution of metal is complicated by passivation. Adding of NH_4Cl to the carbamide is promoted electrical conductivity of fusion, that it is increased to forming of polarization curves on which electrode processes are clearly represented. In carbamide-chloride fusion electrochemical dissolution of rhodium at first flows without limitations, however further there is passivation of anode. The decline of weight for rhodium anode in carbamide-chloride fusion grows in comparison to an individual carbamide, intensity of coloring for fusion increases and arrives at deep yellow-brown color. Electrochemical dissolution of rhodium is accompanied by formation of ions Rh(III).

Anodic dissolution of rhodium was also carried out in acetamide fusion at a temperature 108 °C and fusion of acetamide-NH_4Cl at a temperature 80 °C. Adding of ammoniac chloride to acetamide for formation of eutecticomposition for fusion of acetamide-NH_4Cl (22.3 %) [5] allowed to get polarization curves which clearly represent the electrochemical processes for dissolution of rhodium anode and renewal of his ions. Rhodium dissolves in acetamide-chloride fusion without passivation. Speed of dissolution is $4.70 \cdot 10^{-5}$, that more than in carbamide-chloride fusion, while specific conductivity of fusion carbamide-ammoniac chloride (0,060 Ом$^{-1}\cdot$см$^{-1}$) higher, than acetamide-chloride (0,015 Om$^{-1}\cdot$sm^{-1}) [6]. At dissolution rhodium passes to fusion as ions Rh(III).

The most stable state of oxidization for rhodium is Rh(III) with electronic configuration $[Kr](4d)^6$. For Rh(III) formation of complex connections of octahedral configuration is characteristic. A ground-state for the octahedral complexes of Rh(III) is $^1A_{1g}(t_{2g})^6$, and by the singlet excited state - $^1T_{1g}$ and $^1T_{2g}$, which behave to configuration $(t_{2g})^5$(eg).

In the method of electronic absorption at anodic dissolution of rhenium stripes are fixed in carbamide-chloride fusion - 28000 sm^{-1} and 37000 sm^{-1}, and in acetamide-chloride fusion - 28000 sm^{-1} and 36000 sm^{-1}, in infrared-spectrums of «hard-tempered» samples found out the presence of vibrations $\nu(RH\text{-}N)$ - 480 sm^{-1} and $\nu(Rh\text{-}Cl)$ - 330 sm^{-1}. It characterizes formation in carbamidecompresing and acetamidecomprising fusions of quasi-octahedron complexes of type $[Rh(NH_3)_4Cl_2]^+$ symmetries of D_{4h}.

The values of spectroscopy parameters are got for the complexes $[Rh(NH_3)_4Cl_2]^+$ in carbamide-chloride and acetamide-chloride fusions: $10\ Dq = 31000$ (30650) sm^{-1}; $B =$ 562 (500) sm^{-1}; $b = 0.78$ (0.70). Force of the field of legends is in the mixed complexes $[Rh(NH_3)_4Cl_2]^+$ weaker, than in the cleanly ammoniac complexes $[Rh(NH_3)_4Cl_2]^{3+}$, where $10\ Dq = 33200$ sm^{-1}, that confirms formation in these fusions at anodic dissolution of rhodium for the mixed complexes $[Rh(NH_3)_4Cl_2]^+$.

Determination of kinetic parameters for process of Rh(III) renewal was carried out by the generally accepted method. The basic criteria of difference and convertibility of process were expected according to equations, driven to the monographs of Gallus [7]. It is set that dependence $i_p / V^{0,5} = f(V^{0,5})$ is rectilineal and parallel to abscise axis, that testifies to flowing of process in the diffusive regime, but irreversibly, because dependence of i_p takes place from $V^{0,5}$. Coefficient of diffusion for rhodium ions in carbamide-chloride and acetamide-chloride fusions is conditioned by their conductivity and his value makes $8.4 \cdot 10^{-6}$ sm^2/s for these systems. Renewal of rhodium ions for flows in the diffusive regime to using of the metal.

A size of particles of rhodium sediment is within the limits 10-22 nm. The size of rhodium crystallite is appraised on physical expansion of peaks and makes 5 nm. It testifies to formation in the investigated fusions of nanocomposites of rhodium on the surface of iron, copper and molybdenum. Rhodium coverages, got from fusions on the basis of carbamide and acetamide with a soluble rhodium anode, have a grey color and thickness of 1-6 mcm. At deposition of rhodium as coverage it was got a 0.05-0.70 g of metal depending on time of electrolysis. Thus an output on a current was 85-90 %.

Conclusions. The electrochemical behavior of rhodium in fusions on the basis of carbamide and acetamide is investigated. Anodic dissolution of metal in these electrolytes is accompanied by passivation with formation of complex connections of *Rh*(III), which are restored in the diffusive regime, in one stage, irreversibly to use of the metal. The synthesis of nanoflakes of rhodium and nanocoverages by them iron, copper and molybdenum is carried out.

LIST OF LITERATURE

1. Многофункциональные биосовместимые покрытия на магнитных наночастицах [Текст] / А. В. Бычкова, О. Н. Сорокина, М. А. Розенфельд, А.Л. Коварский // Успехи химии. – 2012. – Т. 81, № 11. – С. 1026-1050.
2. Гусев, А. И. Нанокристаллические материалы [Текст] / А. И. Гусев, А. А. Ремпель. – М. : Физматлит, 2008. – 224 с. – Библиогр. : с. 193-222. – ISBN 5-9221-0039-4.
3. Наночастицы золота, модифицированные координационными соединениями металлов: синтез и применение [Текст] / Е. К. Белоглазкина, А. Г. Мажуга, Р. Б. Ромашкина и др. // Успехи химии. – 2012. – Т. 81, № 1. – С. 65-90.
4. Оленин, А. Ю. Получение, динамика структуры объема металлических наночастиц в конденсированных средах [Текст] / А. Ю. Оленин, Г. В. Лисичкин // Успехи химии. – 2011. – Т. 80, № 7. – С. 535-662.
5. Some new low-temperature melts as electrolytes for electrochemical investigation [Text] / N. Tumanova, O. Bojko, P. Taxill, S. Volkov // International Symposium on Ionic Liquid. – Trondheim – Norway. – 2003. – P. 459-469.
6. Электрохимические свойства расплавов на основе ацетамида как расплавов-растворителей [Текст] / Н. Х. Туманова, О. И. Бойко, Т. В. Трифонова [и др.] // Украинский химический журнал. – 2004. – 70, № 11. – С. 52-55.
7. Галюс, З. Теоретические основы электрохимического анализа [Текст] / З. Галюс. – М. : Мир, 1974. – 552 с. – Библиогр. : с. 547-552.