ELECTRODEPOSITION OF BLACK RHENIUM COATINGS

N. D. Ivanova, N. I. Taranenko, and I. S. Shamina

UDC 541.138.3:546

In the electroreduction of certain transition metal ions from fluoride-containing electrolytes, reduction can be either complete, yielding the metal, or partial, yielding intermediate reduction products at the cathode which, as a rule, represent black coatings, e.g., of chromium, manganese, or molybdenum [1, 2]. We have demonstrated that perrhenate ion reduction can be controlled in fluoride-containing electrolytes. Here, too, one can obtain both bright metallic and compact black coatings. The composition, structure, and properties of the intermediate reduction products must be studied in order to gain an understanding of the mechanism of the complex processes by which the anionic forms of the transition metals are reduced. From a practical point of view, the investigation of these products may lead to new types of coating having specific properties owing to their composition and structure.

It is the aim of the present work to examine the electrodeposition conditions, structure, composition, and properties of black rhenium coatings.

We examined the rate of formation of the intermediate reduction products at the cathode (the weight increase per ampere-hour) as a function of electrolysis parameters: the current density (10 to 220 A/dm^2), the temperature (20, 40, 60, and 80°C), and the fluoride ion concentration (1 to 25 g/liter). Fluoride ions were added to the electrolyte in the form of hydrofluoric acid; the rhenium concentration expressed as metal was varied between 5 and 40 g/liter. The cathode surface area was 0.04 dm^2, the test duration was 15 min in the selection of optimum deposition conditions and 1 h in the collection of black rhenium deposits for analysis of the intermediate reduction products of perrhenate ions. The black coatings were analyzed for the total rhenium content by a known technique [3]. The deviations in parallel tests were ±2%. Each point is the averaged result of five parallel tests. The valence of rhenium in the intermediate reduction products was determined by permanganometry [4]. The average valence was extracted from 5 to 7 parallel measurements.

The rate of formation of the intermediate reduction products is governed chiefly by the fluoride ion concentration, much less by the rhenium concentration in the electrolyte and the electrolysis parameters. The rate of solid-phase deposition is presented in Fig. 1 as a function of fluoride ion concentration at different current densities. It was found that black rhenium coatings are deposited from electrolytes containing 3 to 10 g of metallic rhenium and 1 to 10 g fluoride ions per liter; the electrolysis conditions: temperature 20-25°C, current density 5 to 100 A/dm^2. There is an optimum fluoride concentration with which one obtains maximum deposition rate of black rhenium. It follows from Fig. 2 that the composition of the deposit also is chiefly determined by the fluoride ion concentration. Higher fluoride concentration leads to a higher rhenium concentration in the deposit. The same effect obtains from increasing electrolyte temperature, just as in the case of black chromium [2].

We suggest that like black chromium, the black rhenium as intermediate reduction product of perrhenate ions constitutes a heterogeneous phase containing, in addition to metal, lower-valence rhenium oxide–hydroxide compounds. X-ray phase analysis performed with K_α radiation on a DRON-1 instrument revealed the presence of metallic rhenium with lattice parameters of $a = 2.760$ and $c = 4.458$ Å [5], and that of an additional phase. The valence of rhenium in the intermediate reduction products was found to be three by permanganometry. Thermogravimetric analysis performed with an Orion derivatograph provided evidence for the presence of crystallization water and of OH^- groups. Thus, the thermograms of rhenium samples exhibit endothermic effects at 100-120°C due to the loss of water (3-4%); the next endothermic effect observed at 300°C is caused by elimination of OH^- groups; the weight losses are 3 to 10% (depending on the fluoride ion concentration). Further heating

Institute of General and Inorganic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Élektrokhimiya, Vol. 13, No. 3, pp. 373-375, March, 1977. Original article submitted August 26, 1975. Revised article submitted April 17, 1976.

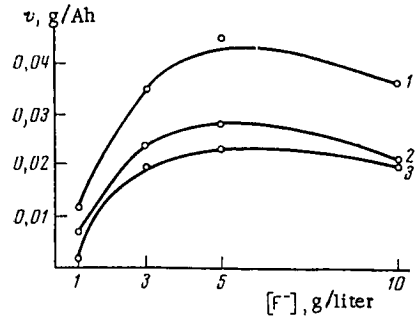

Fig. 1

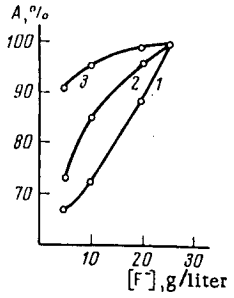

Fig. 2

Fig. 1. The deposition rate of black rhenium (v) as a function of fluoride ion concentration at different current densities: 1) 25, 2) 50, and 3) 100 A/dm^2.

Fig. 2. The amount of rhenium (A) in the deposit as a function of fluoride ion concentration in the electrolyte, at temperatures of 20 (1), 40 (2), and 80°C (3).

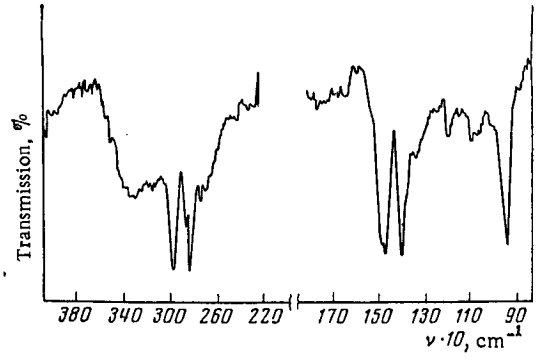

Fig. 3. The IR spectrum of black rhenium.

gives rise to a number of exothermic effects at temperatures between 360 and 450°C (depending on the fluoride ion concentration in the electrolyte); these seem to be due to crystallization of dehydrated product, oxidation of the intermediate reduction products of rhenium, and oxidation of metallic rhenium. The presence of water and of OH^- groups in black rhenium is confirmed by IR-spectroscopic data (4000-400 cm^{-1}). Absorption was found in the region of the bond stretching and deformation vibrations (Fig. 3). Free hydroxyl is characterized by a narrow band with a frequency of 3680 cm^{-1} and deformation vibrations at 937 cm^{-1}. The molecular water is confirmed by the absorption bands ascertained at frequencies of 3218 and 1731 cm^{-1}. In the KBr region there is no absorption which would characterize Me–O bonds, but this does not mean that they are absent. This may be due, both to the undeveloped state of the oxide–hydroxide phase lattice and its significant degree of hydration, and to the high degree of dispersion of the system being examined.

Electron microscopic photography of the black rhenium as powder confirms both the compositional heterogeneity of these deposits and their high degree of dispersion. The grain size is around 10^{-7} cm.

From findings on the way in which the degree of reduction depends on the ratios of the electrochemical reaction rates of the formation of intermediate-valence products and of their reduction to the metal [6], we have developed a new electrolyte for producing black rhenium coatings which has the following component ratios: ammonium perrhenate (expressed as metal) 2-100, hydrofluoric acid 5-50, caustic soda 20-50, and thiourea 0.01-0.1 g/liter. Deposition is recommended to be carried out at pH between 3 and 11, and deposition rates between 0.2 and 0.4 μm/min [7]. The coatings are conducting, and have a high light absorption coefficient: 92-95%. The coatings can be applied directly to copper and its alloys, to molybdenum, and to tungsten.

Thus, it has been established that black rhenium, as the intermediate reduction product of ReO_4^- ions, is a heterogeneous system consisting of metallic rhenium and of lower-valence oxide–hydroxide compounds of rhenium.

LITERATURE CITED

1. N. D. Ivanova and G. A. Alfintsev, Élektrokhimiya, 8, 332 (1972).
2. N. D. Ivanova, K. B. Kladnitskaya, and A. V. Gorodyskii, in: Decorative and Protective Decorative Galvanic and Chemical Coatings [in Russian], Znanie, Leningrad (1973), p. 89.
3. B. S. Tsyvina and N. K. Davidovich, Zavod. Lab., 26, 930 (1960).
4. V. V. Lebedinskii and B. N. Ivanov-Émin, Zh. Obshch. Khim., 13, 256 (1943).
5. I. Swanson and F. Fuyat, N. B. S. Circular, 11, No. 539, 13 (1953).
6. N. D. Ivanova and K. B. Kladnitskaya, Proc. First Ukrainian-Republic Conference on Electrochemistry. Vol. 1 [in Russian], Naukova Dumka, Kiev (1973), p. 145.
7. N. D. Ivanova and N. I. Taranenko, USSR Inventor's Certificate No. 456044, Byul. Izobret., No. 1, 66 (1975).

IODINE DIFFUSION IN $RbAg_4I_5$ AND α-AgI SOLID ELECTROLYTES

V. I. Morozov, V. E. Prokopets, R. P. Sobolev, and F. F. Trush

UDC 621.352.132

The diffusion of iodine in solid silver–iodine electrolytes most often is determined by measuring the current between a silver electrode and an inert electrode in an electrochemical cell of the following type [1-3]:

$$Ag\|RbAg_4I_5\|C(Ti)\|RbAg_4I_5\|I_2(RbI_3),\ C.$$

These measurements are based on the assumption that the short-circuit current between silver electrode and inert electrode is governed by the diffusion flow of iodine which arises in the solid electrolyte layer between the inert electrode and the iodine electrode. However, the diffusion flow of iodine determined by this method cannot always be the true one. The only possibility for measuring the true value of the diffusion coefficient appears to be by applying the radiotracer technique.

We studied iodine diffusion in samples of $RbAg_4I_5$ and α-AgI solid electrolytes using ^{131}I as the radioactive iodine isotope. This was obtained from $Na^{131}I$ solution having an activity of 5.5 mCi by isotope exchange with free iodine followed by ether extraction of the labeled iodine. The specific radioactivity of the iodine obtained was 200 mCi/g. The radioactivity of the samples was measured with an SBT-15 end-window β,γ-radiation counter and PP-15 converter. The samples were first dissolved in water or NH_4I solution, and the radioactivity was counted in a liquid cell placed in a lead housing [4].

Solid-electrolyte pellets of 12 mm diameter and 1 to 4 mm thickness were fabricated from powders by pressing at 4000 kg/cm^2 and temperatures of 25 and 170°C.

Iodine diffusion in $RbAg_4I_5$ solid electrolyte was studied at 25°C in the device shown in Fig. 1. which represented a compression mold (1) with upper (2) and lower (3) die. A thick (4) and a thin (5) electrolyte pellet were placed into the mold, and crystals of radioactive iodine ^{131}I (7) were inserted between them. The gaps were hermetically sealed with fluoroplast [PTFE – Teflon] gaskets (6). The device was placed into an air thermostat with dried air (the humidity was less than 1×10^{-4} g/m^3). The diffusing iodine reacted with the metal, and thus the die (2) served as indicator of iodine diffusion across the upper, thin pellet. The radioactivity of die (2) was checked periodically, and the appearance of radioactive ^{131}I on it was proof that iodine diffused across the upper pellet. The diffusion rate of iodine across the thin electrolyte pellet could be measured by measuring the radioactivity of several upper dies replacing one another. The lower, thick electrolyte pellet (4) was withdrawn from the mold, and the distribution of radioactive ^{131}I across it was examined by abrading thin layers of electrolyte and then counting their radioactivity. The radioactivity of all samples was measured under identical conditions; therefore the true concentration of ^{131}I could be replaced in the calculations by a conventional concentration

Moscow. Translated from Élektrokhimiya, Vol. 13, No. 3, pp. 375-378, March, 1977. Original article submitted October 31, 1975. Revised article submitted May 20, 1976.