Recovery of Cadmium and Change in Properties of a Fibrous Carbon Electrode in Electrolytic Processing of Ammonia Washing Solutions Formed in Cadmium Plating

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Abstract—The possibility of recovering cadmium deposited on fibrous carbon electrodes from ammonium washing solutions formed in cadmium plating via operation of a short-circuited electrochemical system or anodic dissolution was examined. A polarization study of electrode processes that occur on a renewable graphite microelectrode in ammonium solutions of varied composition was carried out. The change in the properties of fibrous carbon electrodes in their cyclic use in electrodeposition–recovery of cadmium and the possibility of their repeated use were analyzed.

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Owing to their specific properties, cadmium coatings are used for protection of articles in aggressive media (high humidity or tropic conditions) [1–3]. Cadmium(II) is to be removed from washing solutions formed in cadmium plating for detoxication of these solutions and recycling of cadmium into the electroplating process. Electrolysis is a way to simultaneously solve these two problems. With account of the low concentration of cadmium(II) in washing solutions, it is preferable to use electrolysis with 3D flow-through electrodes and, in particular, with electrodes made of fibrous carbon materials (FCM) [4].

In the recent decades, electrolysis with fibrous carbon electrodes (FCE) has been successfully used to recover noble and nonferrous metals in hydrometallurgy and electroplating [4, 5]. The use of FCM for electrolytic recovery of nonferrous metals from washing solutions formed in electroplating is due to the necessity for regeneration of carbon electrodes and recycling of the recovered metal into main process. An important issue is that of changes in the FCM properties during their cyclic use in electrodeposition–recovery and of the influence exerted by these changes on the parameters of both the processes. No systematic studies have been performed in this area. The results of previous studies [6–9] suggest that use of FCM in cyclic processes will strongly affect their properties. However, no unambiguous conclusion can be made about whether these changes exert positive or negative influence on the main process of metal electrodeposition because of the scarcity of the available data.

This study was undertaken in order to examine experimentally the possibility of recovery of cadmium deposited on FCE, changes in the FCE properties in an electrodeposition–regeneration cycle, and influence exerted by these changes on the main process for the example of electrolytic processing of washing ammonium solutions formed in cadmium plating.

EXPERIMENTAL

Industrial cadmium-plating ammonium electrolytes of two compositions were chosen for study. Solution no. 1 contained (g l⁻¹): CdSO₄ 50, (NH₄)₂SO₄ 150, H₃BO₃ 25 (pH 5); and solution no. 2: CdSO₄ 50, (NH₄)₂SO₄ 250, urotropin 20, NF dispersant 75 ml l⁻¹ (pH 6) [2, 3]. Supporting electrolytes contained all the components listed above except cadmium. The electrode polarization was carried out using a TES-14 dc power supply in the galvanostatic mode, with the solution circulated by a pmp-304 peristaltic pump through the FCE volume and an intermediate tank at a rate of 0.2 ml cm⁻² s⁻¹ [9]. The solution was delivered to
an electrode with a back current lead from the back side with respect to the counter electrode. The FCE was made of NT-1 carbonized carbon graphite material, its geometric area was 2 cm². A perforated titanium or platinum plate served as a current lead, and a platinum wire, as a counter electrode. To measure changes in the mass and electrical conductivity of the FCE electrode, it was washed with distilled water and dried at 80–100°C. The steady-state electrode potential of a cadmium plate and FCE in the electrolytes were measured relative to a saturated silver chloride reference electrode and recalculated to the hydrogen scale, without drying of the FCE.

The electrical conductivity of FCE was measured with a VM-509 ac bridge and the steady-state electrode potential, with an OR-265/1 pH-meter, using the procedure and setup described in [4]. Polarization curves were measured in the potentiodynamic mode with an RA-2 polarograph on a graphite microelectrode 2 mm in diameter with a surface freshened in the electrolyte solution [10], with a potential sweep rate of 50 mV s⁻¹.

The efficiency of electrolytic recovery of cadmium was evaluated by the degree of recovery, \( \alpha = (c_0 - c_1)\eta c_0 \); current efficiency by cadmium, \( C_E = \frac{[(c_0 - c_1)VF]}{I\tau M_{\text{equiv}}}; \) and electric power consumption \( W = IU\tau/(c_0 - c_z)\). Here \( c_0 \) and \( c_1 \) are the initial and final cadmium concentrations in solution (g l⁻¹); \( V \), solution volume (l); \( F \), Faraday constant (26.8 A h mol⁻¹); \( I \), current (A); \( U \), cell voltage (V); \( \tau \), experiment duration (h); and \( M_{\text{equiv}} \), molar mass of the metal equivalent. The cadmium(II) concentration in solution was determined by the atomic-absorption method.

Figure 1 demonstrates the results of experiments on modeling of the electrolytic recovery of cadmium(II) from a catching bath for an automated cadmium-plating line. A portion of the cadmium-plating electrolyte was introduced at regular intervals of time (15 min) into a solution circulated between the electrolyzer and the intermediate tank, which models a catching bath. The Cd(II) concentration in the solution modeling a single washing of articles changed by 27 to 81 mg l⁻¹. The electrolytic recovery of cadmium(II) was carried out at a current density of 750 A m⁻².

The kinetic curves presented in Fig. 1 reflect the change in the cadmium(II) concentration in a solution before introduction of a portion of the cadmium-plating electrolyte. It can be seen that the time in which a constant cadmium(II) concentration in solution is attained and the level of this constant concentration increase with the amount of the electrolyte introduced in a single washing. The fact that a constant cadmium(II) concentration in solution is reached shows that, under the chosen electrolysis conditions, the whole amount of cadmium(II) introduced in article washing is recovered by electrolysis between two successive washings. Depending on the introduced amount of electrolyte modeling washing of articles with different surface areas, this concentration is 10–35 mg l⁻¹ before deposition of a certain amount of cadmium onto FCE. After that the efficiency of cadmium electrodeposition decreases, which is characterized by an increase in its concentration in solution. Evidently, the main reason for the decrease in the process efficiency is that the reaction surface area and the rate of electrolyte circulation decrease because of the plugging of the pore space in FCE by the deposited metal.

The amount of cadmium deposited per 1 g of FCE varies with the electrolyte composition and is determined by the deposit structure and by the localization of cadmium within the FCE volume, which are governed by specific features of cadmium electrodeposition from the electrolytes under consideration. In the case of metal electrodeposition onto FCM cathodes, the overvoltages of hydrogen evolution on FCM and on a metal being deposited are important for the metal distribution throughout the electrode volume [4]. The overvoltage of hydrogen evolution on cadmium is 1.1 V, and that on graphite, 0.8 V [1, 11]. Therefore, the overgrowth of the electrode with cadmium predominantly occurs on the metal deposited during...