ELECTRODEPOSITION OF THICK, DENSE RHENIUM COATINGS

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Dense galvanic deposits of rhenium on molybdenum and tungsten are of importance in electronics because rhenium prevents secondary emission from these metals and protects them from corrosion in the presence of water vapor. A number of electrolytes and deposition conditions have been proposed [1, 2, 6, 7]. However, only thin rhenium coatings are dense. Thick deposits can be produced by successive deposition with intermediate heat treatment [6] or by deposition of rhenium together with other metals—chromium, for example [2]. It was found earlier [7] that the maximum thickness of good quality rhenium coatings which are dense is 2 μ regardless of the nature of the substrate (molybdenum, tungsten, copper, nickel, or chromium). Neither additional elements introduced into the electrolyte or heat treatment of the coatings leads to an increase of the optimum thickness of rhenium coatings. This led to the conclusion [7] that the mechanism of electrocrystallization of rhenium has some singularities which are not yet known.

The purpose of this study was to find out why thick layers of rhenium do not adhere to the base metal, to elucidate the effect of heat treatment on the adhesion of successive layers of rhenium to each other, and to determine the role of the coprecipitated chromium in the formation of thick (up to 50 μ) dense layers of rhenium-chromium alloys.

Rhenium coatings were deposited on molybdenum from the following electrolytes (g/liter): I) $HReO_4$ (30) + H_2SO_4 (80) + $(NH_4)_2SO_4$ (50); II) $KReO_4$ (12) + H_2SO_4 (80) + $(NH_4)_2SO_4$ (50). The temperature was room temperature and the current density was 20 A/dm^2. The rhenium-chromium alloy was deposited from electrolyte III [$HReO_4$ (30) + H_2SO_4 (80) + $(NH_4)_2SO_4$ (50) + CrO_3 (15)] at room temperature at a current density of 100 A/dm^2. The amount of chromium in the alloy was determined colorimetrically.

EXPERIMENTAL RESULTS

Cathodic Polarization

Substantial cathodic polarization occurs at the lowest current densities at which the metal can be deposited (Fig. 1). The derivative of the current density with respect to the potential increases rapidly after a potential of −0.05 V is reached (with respect to the normal hydrogen electrode).

The hydrogen overvoltage is lower on rhenium than on other metals [8] and at room temperature in a 0.4 N H_2SO_4 solution is equal to 0.14 V and 0.20 V at current densities of 0.1 and 10 A/dm^2 respectively. These results are in good agreement with the results obtained by other investigators [3] and can be explained by the physical nature of rhenium. The interatomic distance in rhenium is a = 2.758 A, which, according to the relationship determined in [4], corresponds to the minimum overvoltage. Such low hydrogen overvoltage may lead to the introduction of hydrogen into the deposit and induce brittleness of thick layers.

Partial polarization curves (Figs. 2 and 3) were determined by weighing the cathode, measuring the volume of hydrogen evolved, and analytical determination of intermediate reduction products in the solution.

Figure 2 shows that in electrolyte I (containing rhenium acid) the discharge of hydrogen ions is facilitated as compared to that in electrolyte II (containing rhenium salt). The co-deposition of rhenium and chromium occurs at more negative potentials than the deposition of pure rhenium and is accompanied by the evolution of a large amount of hydrogen.

TABLE 1. Change of the Volume of the Unit Cell of Rhenium After Heat Treatment

	Annealed metallic rhenium	Electrolytically deposited rhenium	Electrolytically deposited rhenium after heat treatment			
			100°, 12 h, air	250°, 6 h, air	1000°, 10 min, hydrogen	1000°, 15 min vacuum
Volume of the cell, kX^3	28.857	29.984	29.888	29.879	30.490	30.096

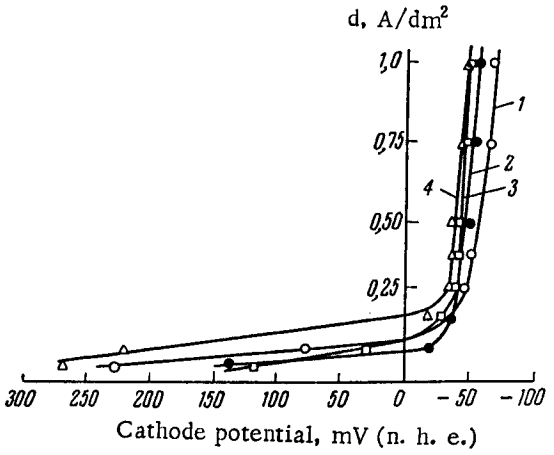

Fig. 1. Cathodic polarization curves of the deposition of rhenium from electrolyte II. Concentration of sulfuric acid (g/liter): 1) 20; 2) 40; 3) 60; 4) 80.

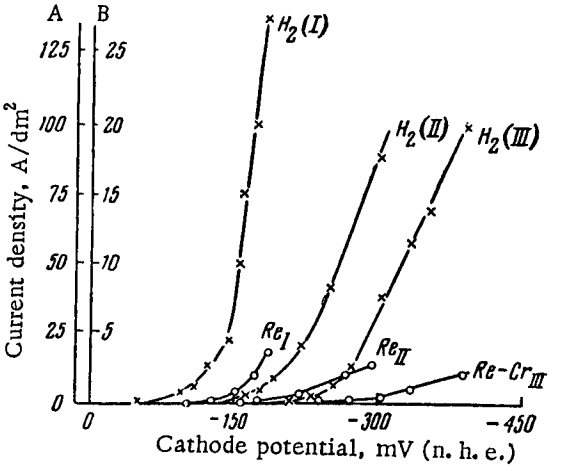

Fig. 2. Dependence of the rate of reduction of ions in electrolytes I, II, and III on the potential. The A axis refers to deposition from electrolyte III; the B axis refers to deposition from electrolytes I and II.

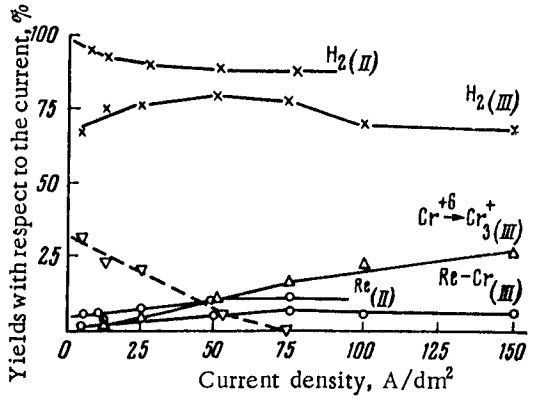

Fig. 3. Distribution of the current in the case of precipitation of rhenium (from electrolyte II) and of the rhenium-chromium alloy (from electrolyte III). The dashed line indicates the formation of rhenium ions of varying valence in electrolyte III (determined by subtraction).

Figure 3 shows that during rhenium plating the whole current within the working range of current densities is distributed between two main reactions: discharge of perrhenate ions and discharge of hydrogen ions (90-95%). During the deposition of the alloy (at current densities between 75 and 150 A/dm^2) a considerable portion of the current (up to 25%) is spent on the intermediate reduction of hexavalent chromium to trivalent chromium; only 60% is spent on the discharge of hydrogen ions.

In order to determine the character of polarization we determined the polarization curves with the NGPK-3M generator at the following rates of change of the current intensity: 1.6, 0.16, and 0.032 A/sec. Measurements were made with a molybdenum electrode which was first coated with rhenium in electrolyte II or III for 1 min. The results obtained show that during rhenium plating as well as during the deposition of the rhenium-chromium alloy the cathodic polarization is chemical and only an insignificant part of the polarization is concentrational polarization. The effective energy of activation was determined at 20-70°C at potential between −0.05 and −0.30 V and was found to be 11,300-14,870 cal/mole, which also confirms the chemical nature of polarization [5].

Heat Treatment

At the present time the only commercial method of obtaining relatively thick layers of rhenium on molybdenum (6-8 μ) consists in successive deposition of layers 1-2 μ thick with intermediate heat treatment at temperatures

TABLE 2. Constants of the Crystal Lattice of Rhenium Coatings on Molybdenum

Nature of the coating / Lattice constant	a kX	c kX	V kX
Rhenium deposited from electrolyte II	2.761	4.542	29.984
Rhenium after heat treatment at 250°C for 6 h in air	2.766	4.496	28.879
Rhenium after heat treatment at 1000°C for 15 min in hydrogen	2.782	4.543	30.490
Rhenium-chromium alloy deposited from electrolyte III	2.759	4.456	29.378

no lower than 800-1000°C for 15-60 min in an atmosphere of hydrogen [6]. Lower temperatures and other media are ineffective. Our many attempts to obtain thick, adherent rhenium coatings in one operation gave negative results under various conditions.

We may assume that the reason for the adhesion of the coating as the result of heat treatment is mutual diffusion of molybdenum and rhenium to a considerable depth. It is also probable that when the rhenium coating is subjected to heat treatment the hydrogen which penetrates the coating during electrolysis is eliminated and that the change in the structure of the deposit makes the adhesion of rhenium possible.

To check these assumptions we made an x-ray analysis of molybdenum samples coated with rhenium. The x-ray photographs were obtained with the RKU-37 and RKU-57-3 cameras with copper radiation and a nickel filter.

The results of these investigations are summarized in Table 1, which shows the variation of the volume of the unit cell of rhenium after heat treatment ($V = 0.865\ a^2c$, where V is the volume of the cell, kX^3; a and c are the lattice constants, kX).

The volume of the cell of rhenium obtained in electrolyte II is larger than the volume of the ideal cell, which can be explained by the penetration of hydrogen. As the result of heat treatment in air at 100 and 250°C, part of the hydrogen is removed from the deposit and the volume of the cell decreases, but this does not ensure the adhesion of a subsequent layer of rhenium to the preceding one. After heat treatment at high temperatures in hydrogen, the volume of the cell increases even with respect to the volume of the deposited rhenium not subjected to heat treatment. This indicates either an additional penetration of hydrogen into the coating from the surrounding medium or the diffusion of molybdenum from the base metal. However, the first hypothesis is impossible, since after heat treatment in vacuum (10^{-4} mm Hg) the volume of the cell remains, as before, somewhat higher than that of the electrolytically deposited rhenium. Apparently, mutual diffusion of the metal of the coating and of the base metal is accompanied by the formation of the rhenium-molybdenum alloy and is the reason for the strong adhesion of the subsequent layers of rhenium to the preceding ones. Since the atomic radii of rhenium and molybdenum are close (the difference is only 1.5%) one can assume that such a considerable change of the volume of the cell results from very strong diffusion.

Investigation of the Crystallization of Rhenium and of the Rhenium-Chromium Alloy

We made an x-ray and electron microscopic analysis of deposits of rhenium and the rhenium-chromium alloy. These analyses led us to certain conclusions about the singularities of the processes of their crystallization and the effect of chromium on the properties and the quality of the alloy.

The influence of chromium on the structure of rhenium is manifest in the decrease of the lattice constant and of the volume of the lattice (Table 2), which indicates the formation of a substitution solid solution and the formation of vacancies.

The degree of imperfection of the structure characterizes to a certain extent the degree of adhesion between the grains of the deposit, i.e., its density. Therefore, we attempted to determine the change in the dislocation density in the rhenium-chromium alloy precipitated on copper by the widening of the fringes on the x-ray diagram [8] obtained in the URS-50I ionization chamber with copper radiation and a nickel filter. The fringes relative to the alloy are much wider than those of electrolytically deposited rhenium. According to the calculations, the average dislocation density for the alloy is $0.44 \cdot 10^{13}\ cm^{-2}$. Such a high dislocation density indicates that the structure

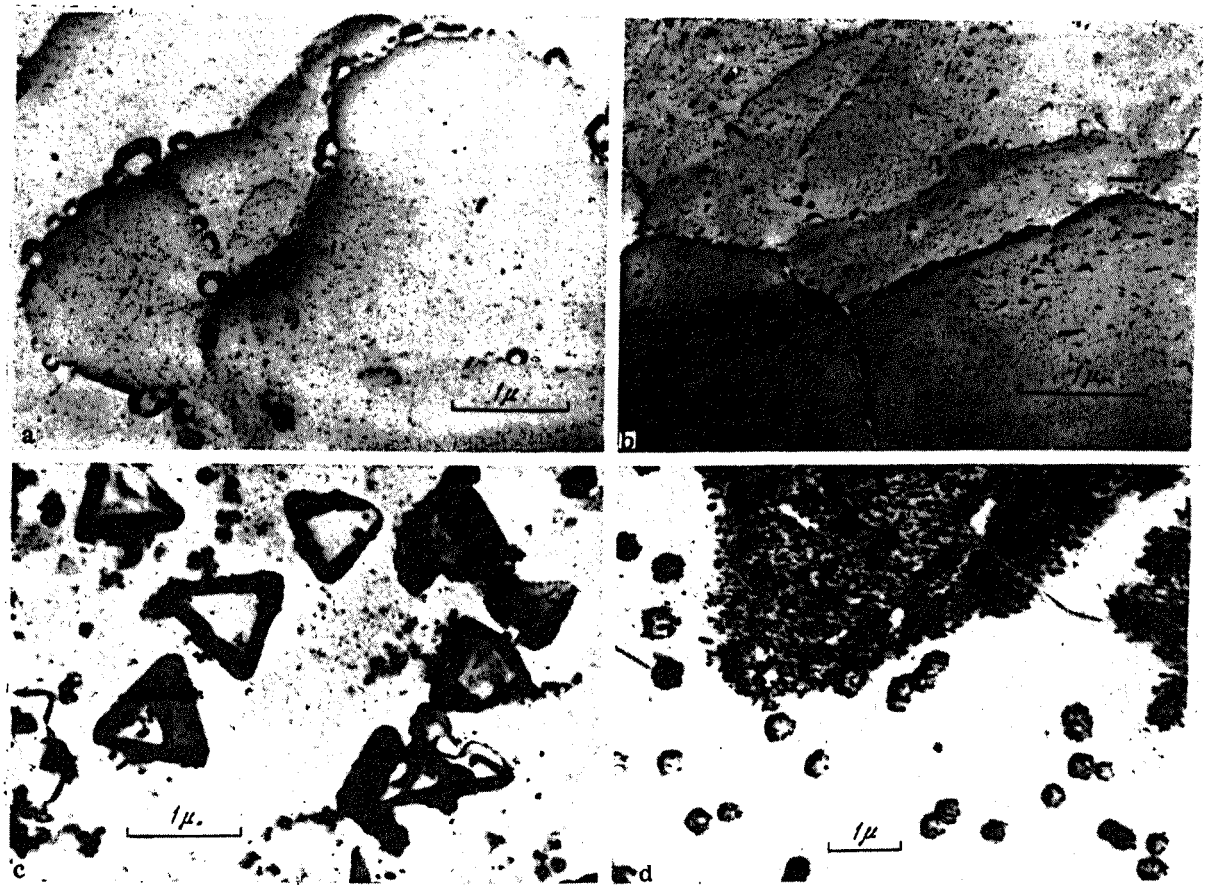

Fig. 4. Photographs of the surface of electrolytic deposits obtained with the electron microscope (×11,400). a) Rhenium, 0.5 μ; b) rhenium, 3.5 μ; c) rhenium-chromium alloy on copper, 10 μ; d) rhenium-chromium alloy on molybdenum, 10 μ. a, b) Obtained from electrolyte II; c, d) obtained from electrolyte III.

of the rhenium-chromium alloy is destroyed. We may assume that the large number of dislocations in the alloy determines the possibility of such a compact crystallization of the alloy in thick layers.

The structure of the upper layer of the coating was studied with the UÉMV-100 electron microscope with a resolution of 10 A under a magnification of 11,400. We used self-shadowed carbon replicas obtained by oblique condensation.

The photographs made with the electron microscope (Fig. 4) show that rhenium is crystallized essentially from somatoid formations with a small number of well formed crystals (Fig. 4a) which are overlapped by the somatoid precipitate when the thickness of the layer increases. At the same time, the coating cracks (Fig. 4b). As a rule, the cracks begin from one large crystal and terminate at another one, i.e., the attachment of the regular crystals to the somatoid precipitate is very weak. X-ray diagrams confirm the implicit crystal structure of rhenium deposits.

The rhenium-chromium alloy (Fig. 4c) precipitates in large well formed crystals which are much larger than in the rhenium deposit and do not overlap as the thickness of the deposit increases. When the thickness of the deposit is 10 μ no cracks occur. However, the dense deposits of the alloy are firmly attached only to the copper or nickel substrate; they do not adhere to the molybdenum, chromium, or tungsten substrate. When the alloy is deposited on molybdenum (Fig. 4d) the structure of the deposit is different. The deposit is much more dispersed and consists essentially of somatoid formations; the larger crystalline precipitates are not localized at the boundaries of the somatoid formation but cover the whole field. The reason for such drastic change in the character of the precipitate is not yet clear, but the lack of adhesion of the alloy to the molybdenum substrate is undoubtedly due to this change.

CONCLUSIONS

1. The lack of adhesion between the base metal and the rhenium coating when the coating is thicker than 2 μ is due to the development of cracks in the coating.

When relatively thick rhenium coatings are obtained by successive deposits of layers 2 μ thick with intermediate heat treatment at temperatures above 800°C in a reducing atmosphere good adhesion is ensured by the formation of the alloy of rhenium and the base metal by diffusion.

3. The influence of chromium in the case of codeposition is due to the formation of a substitution solid solution with rhenium, an increase of the average dislocation density, and precipitation in large regularly formed crystals which increase in size and bind the entire deposit to the base metal.

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