CERTAIN REGULARITIES OF ELECTROCRYSTALLIZATION OF METALS UNDER THE INFLUENCE OF ALTERNATING CURRENT

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INTRODUCTION

In connection with the widespread use of alternating currents in electroplating, it is of interest to study the effect on electrocrystallization of metals, of currents of various forms, obtained through the simultaneous use of direct and alternating voltages in electrolysis. Observations show that the structure of metallic coatings can be sharply changed by alternation of deposition and solution. However, the question of the mechanism of the effect of asymmetric alternating current on electrodeposition has not been adequately clarified in the literature. Among the first works in this field should be noted the works of Stäger [1], Kohlschütter and Schödl [2], N. A. Izgaryshev and S. Berkman [3], N. A. Izgaryshev and N. T. Kudryavtsev [4], V. I. Skirstymonskaya [5], and other authors [6], in which there are indications of a decrease in the polarization and current efficiency for nickel and copper under the influence of alternating current; however, there are practically no data on the structure of deposits obtained under these conditions. In a later work by A. T. Vagramyan and A. A. Sutyagina [7] there is noted a considerable change in the external form, microstructure, and porosity of nickel electrodeposits on superposition of alternating current. Information on the use of alternating current for the purpose of obtaining deposits, in which there is less tension, is given in the cited works [8, 9].

EXPERIMENTAL

In the present work alternating current was supeiposed on direct by means of a previously-described circuit [7] which made it possible to carry out the process with various ratios of alternating- and direct-current components and to vary the frequency of the alternating current in the interval between 50 and 20,000 cycles. The form of the current passing thru the cell was recorded with a loop oscillograph [10, 11]. With a given value of direct current one can obtain at least three different forms of current, which we shall hence forth denote arbitrarily by the terms: 1) $I_{ac} < I_{dc}$ – "rippling current," 2) $I_{ac} = I_{dc}$ – "pulsating current," 3) $I_{ac} > I_{dc}$ – "current with an anodic component" (Fig. 1). We investigated the effect of "pulsating current" and "current with an anodic component" in detail, since, according to preliminary investigations the "rippling current" has no substantial effect on electrocrystallization. Electrodeposition of nickel was investigated in a solution of 160 g/liter of $NiSO_4 \cdot 7H_2O$ + 10 g/liter of NaCl + 30 g/liter of H_3BO_3 at pH 5.6 (I) and also in a solution of the same composition, but with admixtures of various organic substances, in particular 3 g/liter of (2,6 and 2,7)-disulfonaphthalic acid (II) and 0.1 g/liter of thiocarbamide (III).

As an example characterizing the effect of the current, electron micrograms of the surfaces of the nickel deposits are shown below. The deposits shown in Figs. 2a and 3a were obtained with a direct-current density $i_{dc} = 2$ amp/dm^2 from solutions of compositions I and II. Pulsating current has little effect on the structure of the deposit. However, the use of alternating current (50-cycle) having an amplitude greater than the direct current leads to a change in the structure of the deposits. In Figs. 2b and 3b are shown photographs of the surfaces of deposits obtained from solutions I and II, respectively, at $i_{dc} = 2$ amp/dm^2 and $i_{ac} = 7.5$ amp/dm^2.*

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* The alternating-current density was calculated on the basis of absolute values of the strength of the current passing through the cell.

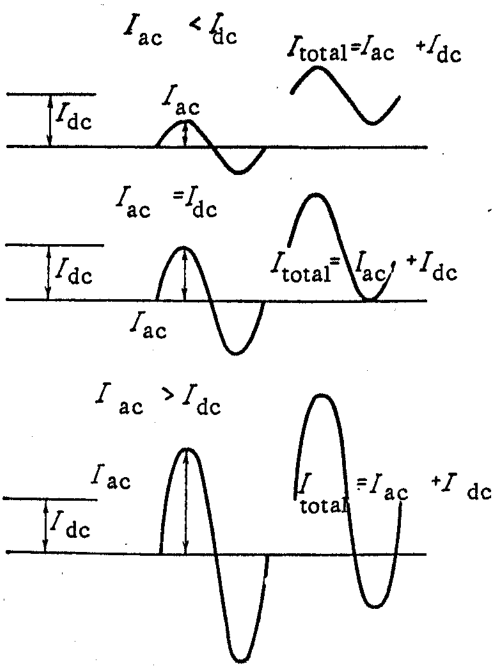

Fig. 1. Schematic representation of the forms of current obtained on superposition of alternating current of various amplitudes on a direct current of fixed magnitude.

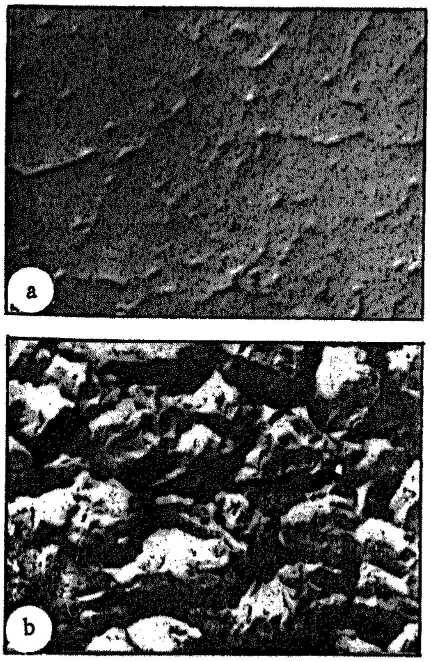

Fig. 3. Surface of a nickel deposit. Electrolyte with an admixture of (2,6 and 2,7)-disulfonaphthalic acid. 16,000 ×. a) i_{dc} = = 2 amp/dm^2; b) i_{dc} = 2 amp/dm^2; i_{ac} = 7,5 amp/dm^2.

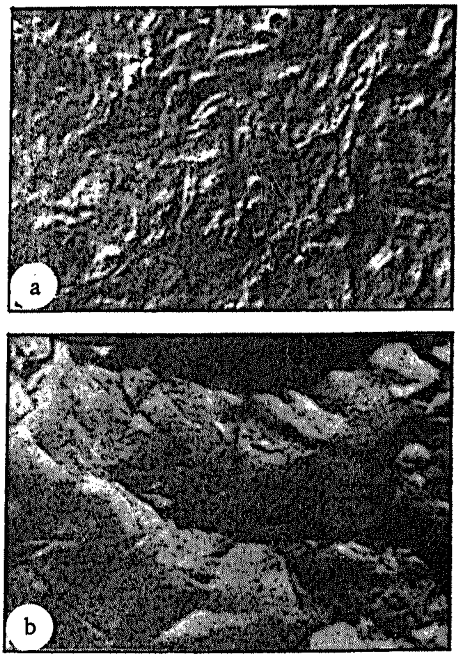

Fig. 2. Surface of a nickel deposit. Electrolyte without admixture. 16,000 ×. a) i_{dc} = 2 amp/dm^2; b) i_{dc} = 2 amp/dm^2; i_{ac} = 7.5 amp/dm^2.

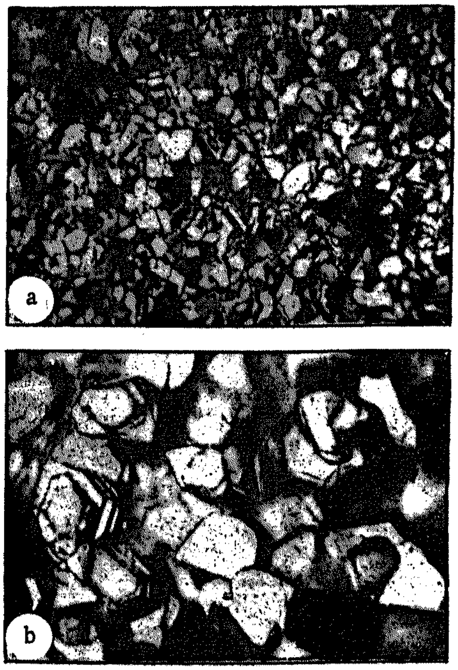

Fig. 4. Surface of a cadmium deposit. Electrolyte with admixture of dextrin. 420 ×. a) i_{dc} = 2 amp/dm^2; b) i_{dc} = 2 amp/dm^2; i_{ac} = 24 amp/dm^2.

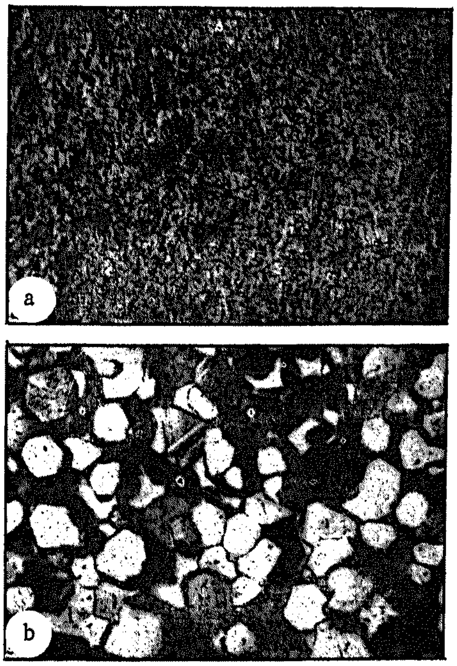

Fig. 5. Surface of a cadmium deposit. Electrolyte with admixture of gelatin. 420 ×. a) i_{dc} = 2 amp/dm^2; b) i_{dc} = 2 amp/dm^2; i_{ac} = 24 amp/dm^2.

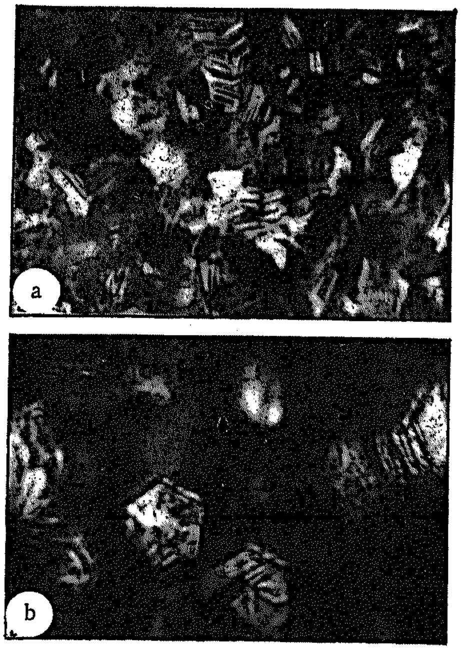

Fig. 6. Surface of a zinc deposit. Electrolyte with admixture of lanthanum sulfate. 420 ×. a) i_{dc} = 2 amp/dm^2; b) i_{dc} = = 24 amp/dm^2.

Cadmium deposits were obtained from the solution: 64 g/liter of $3CdSO_4 \cdot 8H_2O$ + 33 g/liter of $(NH_4)_2SO_4$ + 28 g/liter of $Al_2(SO_4)_3 \cdot 18H_2O$, pH 3.8 (I). On investigating the action of alternating current in the presence of surface-active substances the same electrolyte, with admixtures of either 10 g/liter of dextrin (II) or 0.5 g/liter of gelatin (III), was used.

In Figs. 4a and 5a are shown photographs of the surfaces of cadmium deposits obtained at i_{dc} = 2 amp/dm^2 from baths II and III, respectively. In the case of cadmium, even the use of pulsating current led to changes in the structure of the deposits. However, we observed substantial changes in the structure of the deposits in the case where the ratio i_{ac}/i_{dc} was sufficiently high. In Figs. 4b and 5b are shown photographs of the surfaces of cadmium deposits also obtained from solutions II and III but with i_{dc} = 2 amp/dm^2 and i_{ac} = 24 amp/dm^2 (50-cycle). On comparison of Figs. 4b and 5b it is evident that, as in the case of nickel, the effect of alternating current is manifested primarily by an increase in the crystal size. It should be noted, however, that alternating current has no appreciable effect on the deposition of cadmium from a solution of composition I, without admixtures.

The effect of alternating current on the character of crystallization of zinc was investigated both in pure 2 N $ZnSO_4$ solution (I) and in solutions of the same composition but with admixtures of 0.05-18.6 g/liter of $La_2(SO_4)_3$ (II, 30 g/liter of $Al_2(SO_4)_3$ (III), 10 g/liter of dextrin (IV) and certain other substances as well.

In Figs. 6a and 7a are shown photographs of the surfaces of zinc deposits obtained from solutions II and IV, respectively, at i_{dc} = 2 amp/dm^2. On superposition of alternating current the shapes, sizes, and relative disposition of the crystals change. However, the changes occurring in the structure of the deposits are different in character in solutions with different admixtures. In Fig. 6b is shown a photograph of the surface of a zinc deposit obtained at a ratio i_{ac}/i_{dc} = (24 amp/dm^2)/(2 amp/dm^2) (50-cycle) in a solution of composition II. From Fig. 6b it is evident that the crystals in the deposit are larger than those in the deposit shown in Fig. 6a. Furthermore the crystals in the deposit shown in Fig. 6a are arranged with the basal plane perpendicular to the surface, while in the deposit shown in Fig. 6b, the basal planes lie parallel to the surface. A similar picture is observed in deposits obtained from solutions I and III.

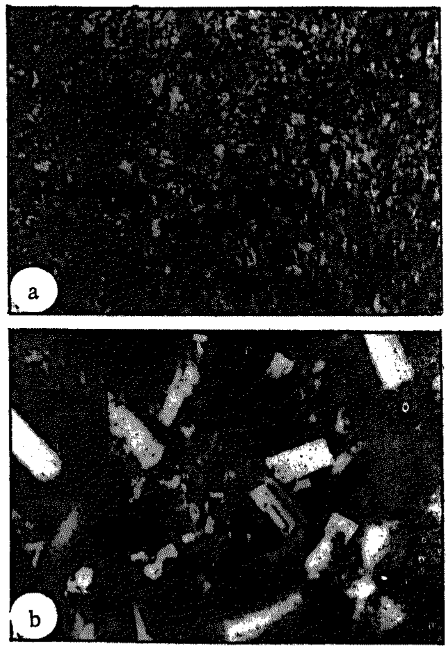

Fig. 7. Surface of a zinc deposit. Electrolyte with admixture of dextrin. 420 ×. a) i_{dc} = 2 amp/dm^2; b) i_{dc} = 2 amp/dm^2; i_{ac} = 24 amp/dm^2.

In contrast to the cases described, for deposits formed in solutions containing dextrin the superposition of alternating current (50-cycle) in the ratio indicated above leads to a considerable increase in the dimensions of the crystals; however, their shape proves to be entirely different. In Fig. 7b is shown a photograph of the surface of a zinc deposit obtained from solution IV at i_{ac}/i_{dc} = (24 amp/dm^2) (2 amp/dm^2) (50-cycle). On comparison of Figs. 6b and 7b it is evident that the faces extending parallel to the surface in the latter case are not basal planes but prism faces.

It is of interest to note that as a result of superposition of alternating current, the relative deposition of the crystals changes; in this case there is observed the appearance of texture along the cube axis [001] for nickel and the hexagonal axis [001] for zinc and cadmium.

Changes in the structure of the deposits taking place under the influence of 50-cycle alternating current gradually diminish as the frequency of the latter increases, and completely vanish when nickel is deposited from solution I at a frequency of 500 cycles and from solution II at 5000 cycles, or when cadmium is deposited from solutions I and II at 12,000 cycles. In the case of zinc deposition the changes occurring under the influence of alternating current vanish at a frequency in the interval 400-2000 cycles, depending on the nature of the admixture. The dependence of the degree of the influence of the alternating current on its frequency apparently indicates that the rates of the processes occurring at the cathode under these conditions are limited.

It should be noted that on superposition of alternating current, cadmium and zinc deposits, in which the texture in the direction of the hexagonal axis [001] matched the configuration of the surface, were obtained for the first time, despite the laws of formation of "growth texture" by the basal planes. When the crystals are closely packed, this combination leads to the formation of a surface with a high reflection coefficient. The causes of this crystal growth have been considered by us [11] on the basis of the work by Kaischew and Bliznakow [12] on the growth of homopolar-type crystals on a structureless base.

DISCUSSION OF RESULTS

In analyzing the effect of the current flowing in the reverse direction—the "anodic current" — on electrocrystallization, one should take into account firstly, the possibility of a change in the conditions of adsorption of surface-active admixtures and in their nature, secondly, the possibility of surface activation, and thirdly, the increase in the concentration of ions of the metal being discharged, which takes place at the electrode.

Comparison of the potential values, which we obtained on superposition of alternating current, with zero-charge potential values of the investigated metals, given in the literature, however, does not provide grounds for explaining the results on the basis of desorption phenomena. Supplementary investigations by us of the adsorption of thiocarbamide on nickel from a solution of composition III, with the aid of a radioactive isotope of sulfur (S^{35}) confirmed by hypothesis that desorption of an admixture does not occur on superposition of alternating current of the amplitudes indicated in the experimental part. Study of the shapes of crystals formed under the influence of alternating current in solutions containing surface-active substances showed that they are not similar to the shapes of crystals formed under the same conditions in a solution without admixtures. This also indicates that the effect of alternating current on crystallization cannot be due entirely to the desorption of surface-active substances.

The observed effects can be more satisfactorily explained by taking into account the changes in concentration of the ions being discharged and the change in the activity of the surface. Thus it was found [11] that in the deposition of zinc in the presence of superposed alternating current ($i_{ac}/i_{dc} > 1$) the potential has, for a certain time, a value more positive than the stationary electrode potential in the given solution. The increase in the concentration of zinc ions at the electrode due to solution is apparently insufficient to give rise to new nuclei, since the duration of current flow in the anodic direction in each period does not exceed 1/100 second. Besides, solution may activate the surfaces of the crystal faces, metal being deposited on the faces of the same crystal in the following stage as a result.

In contrast to the cases of zinc and cadmium, when nickel is deposited in the presence of superposed alternating current, the potential does not reach values at which the nickel dissolve. The causes of monotypic changes in the structure of nickel deposits, regardless of the nature of the admixture in the solution, apparently may be connected with a change in the conditions of formation of the hydroxide and inclusion of the latter in the deposit. In the literature there are indications both of inclusion of the hydroxide in nickel deposits [13] and of its presence on the surface of bright nickel deposits [14, 11]. On the surface of deposits formed in solutions with the same admixtures in the presence of superposed alternating current ($i_{ac}/i_{dc} > 1$), the hydroxide was not found. Electronograms provide clear diffraction patterns corresponding to metallic nickel. The observed potential decrease and greater size of crystals in deposits obtained at $i_{ac} / i_{dc} > 1$ further indicate that the role of the OH^- in the deposition process is less in this case. Quite understandably, the content of hydroxide in the deposit may decrease owing either to its formation being hindered or to conditions which prevent its inclusion in the deposit (coagulation, etc.).

We advanced the hypothesis [11] that under the electrical conditions established at the electrode, ionization of hydrogen adsorbed on the deposit or present in the form of the hydride occurs. As a result of this reaction H^+ ions accumulate right at the electrode, owing to which formation of the hydroxide and, hence, its inclusion are hindered. The following facts, established by us, may be adduced in favor of the stated hypothesis on the character of the anodic process: a) alternating current has no effect on the size of crystals in nickel deposits obtained from acid electrolytes ($pH \leq 2$); b) on superposition of alternating current the amount of hydrogen, included in the deposit decreases, and the periodicity usually observed in the structure of the deposit (stratification of the deposit), is disturbed; the layers become less pronounced and are more widely separated from one another; c) the content of sulfur in nickel deposits increases under the influence of alternating current, as it does when the acidity of the solution is increased.

It should be noted, however, that the texture of deposits obtained from acid electrolytes ($pH \leq 2$) differs from that of deposits obtained on superposition of alternating current. Besides, the decrease in the current efficiency for nickel observed under these conditions is not in accord with the mechanism of the influence of alternating current proposed for nickel. Possibly, when additional data are obtained on the conditions of formation and the behavior of the hydroxide right at the cathode under the influence of alternating current, the noted contradiction will be resolved.

From all that has been set forth it is evident that the observed influence of alternating current on the structure of deposits, with its frequency dependence, opens up certain new possibilities for the study of factors affecting the electrocrystallization of metals.

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