

EFFECT OF CRYSTALLOGRAPHIC SURFACE INHOMOGENEITY OF POLYCRYSTALLINE ELECTRODES ON ANION ELECTROREDUCTION KINETICS

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UDC 541.138

The effect of crystallographic surface inhomogeneity of polycrystalline electrodes on anion electroreduction kinetics was examined. It was shown theoretically that corrected Tafel plots for the reduction of anions of the $S_2O_8^{2-}$ type should not coincide for different polycrystalline electrodes with pronounced crystallographic surface inhomogeneity. An analysis of experimental data for the polycrystalline silver electrode fully confirms this result.

It is one of the important problems of electrode kinetics to study the rates of electrochemical reactions as functions of the electrode type. The electroreduction of anions of the $S_2O_8^{2-}$ type (anions of the first group [1]) can be examined as a convenient model for finding out the reasons of such a dependence. The quantitative theory resting on the assumption that the elementary act of the reaction occurs with a certain finite rate was put forward by Frumkin [2-5]. According to this theory, the reaction rate is related to electrode potential, E , by the equation

$$i = K c_A \exp \left[\frac{\alpha F}{RT} \left(-E + \frac{n_1 + \alpha}{\alpha} \psi_1 \right) \right], \quad (1)$$

where K is the reaction rate constant, c_A and n_1 are the concentration and charge of the reacting species in the bulk solution, α is the transfer coefficient, and ψ_1 is the average value of potential in the plane of the centers of charge of the reacting species in the transition state of the reaction.

The theory rests on the following assumptions. During current flow, the equilibrium distribution of the concentrations of all ions and, accordingly, that of the electrode potential in the diffuse layer is not upset, and corresponds to Gouy-Chapman theory; the structure of the electrode's electric double layer obeys the theoretical relations of Grahame's model; noncoulombic interactions of the reacting species and reaction products with the electrode surface and with the ions of the electric double layer are independent of potential; the anions are discharged from a position at the outer Helmholtz plane, i.e., $\psi_1 = \psi_0$ (ψ_0 is the potential of the outer Helmholtz plane), and therefore, the discreteness-of-charge effect in the diffuse part of the double layer is not taken into account; and the relation between the rate of the reaction involving the adsorbed species $\left(\ln i + \frac{n_1 F}{RT} \psi_0 \right)$ and

the effective potential difference ($E - \psi_0$) is described by Tafel's classical equation with constant coefficient α . It has been shown for a large number of reactions involving the reduction of anions of the first group [5-12] that the theory of slow discharge quantitatively describes the reaction rate as a function of electrode potential, base-electrolyte type, and base electrolyte concentration. The dependence of discharge rate on the metal type has been analyzed in detail in a number of papers [13, 14], and it was found that the rate constant of electrochemical reactions to which the Brønsted relation can be applied does not depend on the electrode type, provided the potential is reckoned from some standard reference electrode. This is due to the fact that for $E = \text{const}$, the chemical-potential difference of the electron in two different metals is balanced by the Galvani-potential difference at the interface of both metals with the solution. The energy level of the electron relative to the solution and, hence, the (real) activation energy of the reaction turn out to be identical for different electrodes [15]. In this case, any differences in the rates of anion discharge at different metals and, exactly so, at different crystallographic faces of a given metal solely arise from corresponding changes in electric double-layer structure, i.e., changes in the ψ_0 -potential, the size and sign of which are governed by the position of the electrode's potential of zero charge (p.z.c.) and by the values of capacity of the compact double-layer part.

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It follows when Eq. (1) is rewritten as

$$\ln i + \frac{n_i F}{RT} \psi_0 = \ln K c_A - \frac{\alpha F}{RT} (E - \psi_0) \quad (2)$$

that plots of reaction rate against potential constructed as $\left(\log i + \frac{n_i F}{2.3RT} \psi_0\right)$ against $(E - \psi_0)$, known as corrected Tafel plots (CTP), are linear and coincide for different base-electrolyte concentrations and for different electrode types.

This conclusion was quantitatively confirmed when studying the electroreduction of anions $S_2O_8^{2-}$, $S_4O_6^{2-}$, and $Fe(CN)_6^{3-}$, both at electrodes with a homogeneous surface (liquid electrodes, single-crystal faces) and at polycrystalline electrodes in aqueous and nonaqueous solutions [5-12]. The only exception found were the data for the reduction of anion $S_2O_8^{2-}$ at polycrystalline silver [16], where the CTP did not coincide with those for silver single-crystal faces (111) and (100) and for other solid polycrystalline electrodes examined.

The suggestion was made in [16] that the characteristic differences between the CTP for polycrystalline silver and other electrodes can be attributed to substantial crystallographic surface inhomogeneity [17, 18] of this electrode arising from considerable differences in the p.z.c. of the individual silver single-crystal faces. The detailed analysis [19] of crystallographic surface inhomogeneity and its effect on electric double-layer structure at polycrystalline electrodes yields quantitative criteria for its effect on anion electroreduction kinetics.

In terms of models for the structural surface properties of these electrodes, where the surface represents a set of individual single-crystal faces, two possible schemes of combination of diffuse-layer capacity have been discussed in [19]: (i) Each face has its own compact and diffuse double layer (model I), and (ii) the faces retain their own characteristic compact layers, but the diffuse part of the double layer is common to both faces (model II). One can readily see that in model I, the charge distribution in the diffuse double-layer part is nonuniform, so that the outer Helmholtz plane is nonequipotential.* In model II, to the contrary, the polycrystalline electrode, like electrodes with a homogeneous surface, has an equipotential outer Helmholtz plane.

It follows from Eq. (1) that a decrease in the rate of anion discharge at the negatively charged electrode surface to a first approximation is due to the dependence of ψ_0 -potential on polarization and on the concentration of indifferent electrolyte in the solution [1, 5-12]. Hence the ratio between the reaction rates at polycrystalline electrodes operating according to model II and at electrodes with a uniform surface will only depend on the differences in the average values of compact-layer capacity at $(E - \psi_0) = \text{const}$ and on the difference in zero-charge potentials. The reaction rate constant K and the transfer coefficient α remain unchanged here.

A basically different effect can be expected when the anions are discharged at the surface of a polycrystalline electrode where electric double-layer structure follows the relations of model I. In fact, at a given value of electrode potential E relative to a constant reference electrode, the outer Helmholtz plane close to which are located the electric centers of the discharging species is nonequipotential, and hence the reaction rates at different surface sections are not the same. Under these conditions the values of K and α formally can undergo strong changes as one goes from a uniform to a polycrystalline surface structure of the electrode, and the CTP for the anion reduction reaction will not coincide.

CALCULATING PROCEDURE

The calculation was performed on the assumption that two thermodynamic equilibrium faces, (1) and (2), are exposed at the surface of the polycrystalline electrode. Property changes in the border regions were disregarded. Face (2) is more hydrophilic than face (1), i.e., $(C_H^{(2)})_{q=0} > (C_H^{(1)})_{q=0}$, where C_H is the compact-layer capacity of the corresponding face. For large negative potential drops in the compact double-layer part we have $C_H^{(2)} = C_H^{(1)}$, and the values do not change when cathodic polarization is further increased. The zero-charge potential of face (1), $E_{q=0}^{(1)}$, is 0.233 V less negative than the p.z.c. of face (2), $E_{q=0}^{(2)}$, which is due to their

*We disregard nonequipotentiality of the outer Helmholtz plane arising from the discrete character of ion distribution in the diffuse layer. This does not have any effect on all subsequent results, however, since a certain parallelism was found to exist in the relations between the local value of ψ_1 -potential and the mean value of ψ_0 -potential as functions of electrode potential E and base-electrolyte concentration [8].

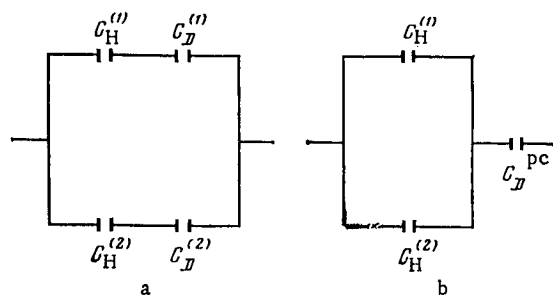


Fig. 1. The electric equivalent circuits of models I (a) and II (b).

different hydrophilicities.[†] The crystallographic inhomogeneity of the electrode was assumed to be maximal, i.e., $\theta^{(1)} = \theta^{(2)} = 0.5$ where $\theta^{(1)}$ and $\theta^{(2)}$ are the surface fractions taken up by faces (1) and (2), respectively.

First we specified the partial C_H vs. q curves of faces (1) and (2) with parameters close to those found experimentally in aqueous solutions. According to the electric equivalent circuit for model I (Fig. 1a), the capacity of the polycrystalline electrode, C^{pc} , at $E = \text{const}$ is given by,

$$C^{pc} = 0.5[C^{(1)} + C^{(2)}]. \quad (2)$$

To find the compact-layer capacity of the polycrystalline electrode, C_H^{pc} , as a function of the potential drop in the compact layer ($E - \psi_0$), one must know the values of $C_H^{(1)}$ and $C_H^{(2)}$ at the same potentials. For face (1), the potential ($E - \psi_0$) corresponding to charge q was determined from the relation

$$(E - \psi_0) = \int_0^q 1/C_H^{(1)} dq, \quad (3)$$

while that for face (2) is determined by

$$(E - \psi_0) = (E - \psi_0)^* - \int_{q^*}^q 1/C_H^{(2)} dq, \quad (4)$$

where $(E - \psi_0)^*$ is the potential drop in the compact double-layer part which corresponds to the charge, q^* , where the partial C_H vs. q curves merge.

To calculate the differential capacity of the polycrystalline electrode as a function of potential in solutions of different concentration one must know capacities $C^{(1)}$ and $C^{(2)}$ as functions of E in the same solutions. Hence the fundamental relation of Grahame's theory,

$$1/C = 1/C_H + 1/C_D, \quad (5)$$

where $C_D = 19.45\sqrt{137.8c + q^2}$, was used to find values of $C^{(1)}$ and $C^{(2)}$ for $q = \text{const}$. The change from charge to potential for the two faces was accomplished via relations similar to (3) and (4). For face (1),

$$E = \int_0^q 1/C^{(1)} dq \quad (6)$$

and for face (2),

$$E = E^* - \int_{q^*}^q 1/C^{(2)} dq, \quad (7)$$

where

$$E^* = \int_0^{q^*} 1/C^{(1)} dq. \quad (8)$$

The potential dependence of capacity of the polycrystalline electrode in solutions of different concentrations was found from relation (2). To calculate the ψ_0 -potential we evaluated the value of charge q corresponding to electrode potential E via the equation

[†]The neglect of different work functions of faces (1) and (2) is inconsequential for further results when the electrode charge is reckoned from the value of charge corresponding to the potential of the minimum ($E_{\min}$) in the C^{pc} vs. E curve.

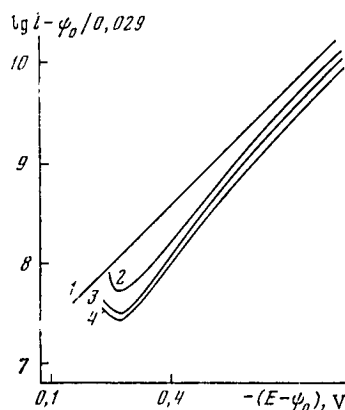


Fig. 2

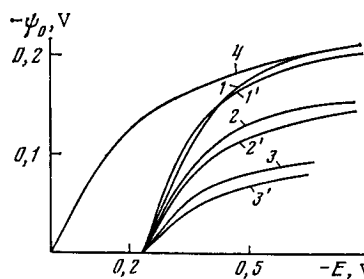


Fig. 3

Fig. 2. Corrected Tafel plots for the reduction of divalent anions: 1) at faces (1) and (2), 2) to 4) at the polycrystalline electrode in the presence of different concentrations of the indifferent base electrolyte: 2) 0.001 M, 3) 0.01 M, and 4) 0.1 M.

Fig. 3. The ψ_0 -potentials as functions of electrode potential E: 1) to 3) and 1') to 3') at the face (2) and at the polycrystalline electrode, with concentrations of the indifferent electrolyte of: 1) and 1') 0.001 M, 2) and 2') 0.01 M, 3) and 3') 0.1 M, 4) at face (1) for a concentration of 0.001 M.

$$q = q^* - \int_{x^*}^x C^{pc} dE. \quad (9)$$

It is usually assumed when analyzing the experimental plots of double-layer capacity against potential for a polycrystalline electrode that the surface charge is zero in the minimum of the C vs. E curve in dilute electrolyte solutions.* Hence in the calculations performed in the present work, electrode charge also was reckoned from the charge corresponding to E_{min} .

The average value of the ψ_0 -potential for $q < 0$ was calculated from diffuse double-layer theory:

$$\psi_0 = -0.0513 \operatorname{arcsh}(q/11.72\bar{V}c). \quad (10)$$

The numerical values in Eq. (10) correspond to aqueous solutions of surface-inactive electrolytes at $T = 25^\circ\text{C}$.

Average values of reaction rate at the polycrystalline electrode at $E = \text{const}$ were determined from the relation

$$i_{pc} = 0.5[i^{(1)} + i^{(2)}], \quad (11)$$

where $i^{(1)}$ and $i^{(2)}$ are the partial discharge currents at the corresponding faces, while the currents at the individual faces were calculated via Eq. (1) with $n_1 = -2$.

CALCULATED RESULTS AND DISCUSSION

A straight-line CTP for electroreduction of a divalent anion (Fig. 2, straight line 1) with a slope of $\alpha = 0.23$ was specified as starting point [1, 5]. Then Eq. (10) was used for three solution concentrations (0.1, 0.01, and 0.001 M) to find ψ_0 vs. E relations for the individual single-crystal faces [Fig. 3, curves 1 to 3 for face (2), curve 4 for face (1)]. For a calculation of the partial discharge currents, $i^{(1)}$ and $i^{(2)}$, as functions of electrode potential E (Fig. 4, curves 1 and 2 for 0.001 M solution), the values obtained for the ψ_0 -potential were substituted into Eq. (1). Figure 4 also shows the plot of discharge rate against potential E for the polycrystalline electrode calculated via Eq. (11).

The rates of anion electroreduction thus found were corrected for the effective values of the ψ_0^{pc} -potential calculated via Eq. (10) for the polycrystalline electrode. The calculated ψ_0^{pc} vs. E relations are reported.

*It had first been observed in [18] that actually, at E_{min} the average surface charge of a polycrystalline electrode operating according to model I is not zero but can attain appreciable negative values [19].

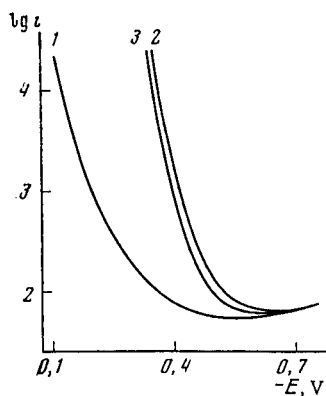


Fig. 4

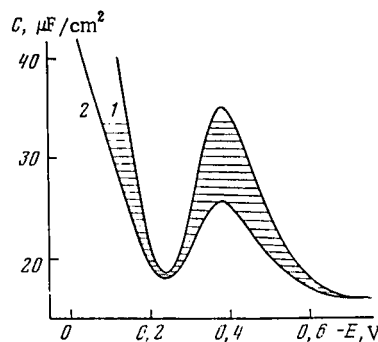


Fig. 5

Fig. 4. The reduction rates of divalent anions as functions of electrode potential: 1) at face (1), 2) at face (2), and 3) at the polycrystalline electrode.

Fig. 5. Differential capacity as a function of electrode potential in 0.01 M solution of an indifferent electrolyte: 1) at face (2), 2) at the polycrystalline electrode.

in Fig. 3. One can see from this figure that $\psi_0^{\text{PC}} = \psi_0^{(2)} = 0$, only for $E_{q=0}^{(2)} = -0.233$ V, in accordance with the adopted way of reckoning the charge of the polycrystalline electrode. At all other values of E one has $|\psi_0^{\text{PC}}| < |\psi_0^{(2)}|$, except for very dilute solutions (0.001 M) for which $|\psi_0^{\text{PC}}| > |\psi_0^{(2)}|$ when the potential is slightly more negative than $E_{q=0}^{(2)}$. This inversion of the inequality arises since the capacity of the polycrystalline electrode close to $E_{q=0}^{(2)}$ does not tend toward zero with increasing dilution of the solution, as it does at electrodes with a uniform surface, but toward some limiting value depending, in general, on the surface fraction of the faces and on the differential capacity of face (1) at the p.z.c. of face (2) [18, 19]. In more concentrated solutions one always finds $C^{\text{PC}} < C^{(2)}$ for $E = \text{const}$, so that $|q^{\text{PC}}| < |q^{(2)}|$, and in accordance with relation (10), $|\psi_0^{\text{PC}}| < |\psi_0^{(2)}|$.

The CTP calculated for the electroreduction of divalent anions for three solution concentrations are presented in Fig. 2 (curves 2, 3, and 4). An analysis of the shape of these curves and of their dependence on base-electrolyte concentration leads to the conclusion that in the CTP for the polycrystalline electrode, in contrast to that for electrodes with uniform surfaces, three regions with substantially different values of α^{PC} are present.

Close to $E_{q=0}^{(2)}$ the transfer coefficient α^{PC} assumes negative values. This result can be explained with the aid of Fig. 5, which reports the C vs. E curves for face (2) and for the polycrystalline electrode in 0.01 M solution of a surface-inactive base electrolyte. The shaded area corresponds to the surface-charge difference of the two electrodes at $E = \text{const}$. When the potential is displaced from $E_{q=0}^{(2)}$ in the direction of more negative values, the absolute value of $|q^{(2)}|$ increases more strongly than that of $|q^{\text{PC}}|$ (Fig. 6). In other words, the effective repulsion of the anions at the negatively charged surface is smaller for the polycrystalline electrode than for face (2), and the values of $\log i^{\text{PC}}$ corresponding to the polycrystalline electrode thus are "undercorrected" for the ψ_0 -potential.

Starting from $E = -0.353$ V (a minimum is seen at this value of potential in the CTP of the polycrystalline electrode in 0.01 M solution), the absolute value of the charge difference, $|q^{(2)} - q^{\text{PC}}|$, increases more slowly (Fig. 6), and the polycrystalline electrode surface begins, formally, to repel anions more strongly. In other words, in this potential range, the values of $\log i^{\text{PC}}$ for this electrode are, as it were, "overcorrected" for the ψ_0 -potential, which is responsible for the approximately linear section appearing in the central part of the CTP where the α^{PC} value is substantially higher than that at single-crystal faces.

At potentials more negative than the point of merger of the C vs. E curves of faces (1) and (2), the difference between the values of charge of face (2) and the polycrystalline electrode attains a constant value, and hence the CTP for the polycrystalline electrode becomes parallel to that for the single-crystal faces. The formal decrease in reaction rate constant which occurs as one goes from the single-crystal faces to the polycrystalline electrode is due to the reference point selected in reckoning the charge of the crystallographically inhomogeneous surface.

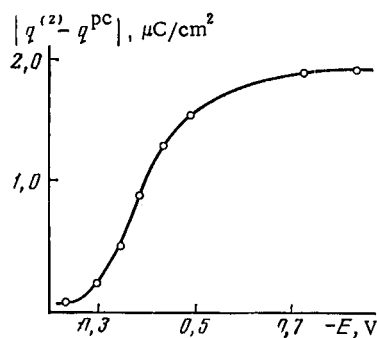


Fig. 6. The absolute value of the surface-charge difference between face (2) and the polycrystalline electrode, $|q^{(2)} - q^{PC}|$, as a function of electrode potential E .

It follows from Fig. 2 that in contrast to the single-crystal faces, the CTP for the polycrystalline electrode depend on concentration of the indifferent electrolyte. This result arises since the concentration of ions in the diffuse double-layer part changes, not only with distance from the surface of the polycrystalline electrode but also in a direction parallel to this surface. Therefore, the one-dimensional diffuse-layer model of Gouy and Chapman is found to be inapplicable for the polycrystalline electrode [19].

ANALYSIS OF THE EXPERIMENTAL DATA

It had been shown in [19] that crystallographic surface inhomogeneity is peculiar to all polycrystalline electrodes, at least to some extent, but the effect is largest for gold and, particularly, for silver. Under this aspect we shall attempt to analyze the kinetics of persulfate ion electroreduction at silver single-crystal faces with the Miller indices (111) and (100)* and at polycrystalline silver. The corresponding data are reported in [16].

Figure 7 reproduces CTP for persulfate ion reduction obtained at a number of polycrystalline electrodes, at silver single-crystal faces, and at polycrystalline silver. For the construction of CTP of polycrystalline silver in [16], the corresponding ψ_0^{PC} vs. E relations were calculated from the C^{PC} vs. E curves of [20] using the roughness factor $f=1.3$ reported in that work.† It was shown in later work, however [21], that $f=1.5$. That f cannot be 1.3 also follows from our analysis. One can see from Fig. 2 that at the negatively charged surface of the polycrystalline electrode, the anion electroreduction rate corrected for the ψ_0 -potential always is lower than that at the single-crystal faces, while the CTP calculated with $f=1.3$ for the polycrystalline electrode intersects the CTP for the single-crystal faces (Fig. 4 in [16]).

The CTP of polycrystalline silver shown in Fig. 7 was calculated with $f=1.5$. This figure shows that the CTP for the silver single-crystal faces and for polycrystalline electrodes of bismuth, tin, and lead coincide. The lack of any important effect of crystallographic surface inhomogeneity of these electrodes on the reaction kinetics appears to be due to the small p.z.c. anisotropy of the single-crystal faces of these metals. But the experimental data for polycrystalline silver can be explained in terms of the analysis performed in the present work.

One can see when comparing Figs. 2 and 7 that the CTP of polycrystalline silver can be identified with the central section of the calculated curve characterized by a substantial increase in the value of α^{PC} and the gradual transition to a potential region where the CTP for the polycrystalline electrode and the single-crystal faces are parallel.‡

*The electroreduction kinetics of this anion has not been studied at the (110) face of silver single crystals.

†Actually the reciprocal slope of the plot of Parsons and Zobel for the polycrystalline electrode $f=f_R f_{CI}$, where f_R is the roughness factor while f_{CI} is the factor of crystallographic surface inhomogeneity [17, 19].

‡It follows from the above analysis that the variation of α with electrode potential is due to crystallographic surface inhomogeneity of the polycrystalline electrodes and cannot be used as evidence for the dependence of α on E predicted by quantum-mechanical theory of the elementary act [22].

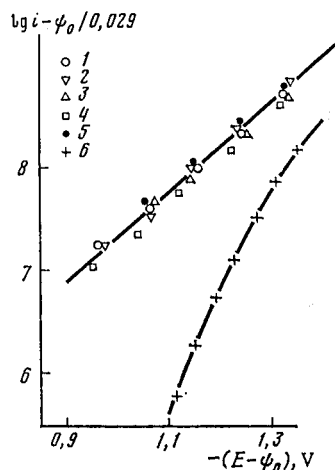


Fig. 7. Corrected Tafel plots for the reduction of 10^{-3} N $K_2S_2O_8 + 0.9 \cdot 10^{-2}$ N KF at the electrodes: 1) Bi, 2) Sn, 3) Pb, 4) Ag-(111), 5) Ag(100), 6) polycrystalline Ag.

The lack of a section with minimum ($\alpha^{PC} < 0$) in the experimental curve can be explained by arguing that the real reaction rate at the polycrystalline electrode close to the potential of the minimum in the C^{PC} vs. E curve is lower (probably because of oxidation) than expected from the model discussed. It also can be understood that the CTP for persulfate ion reduction obtained at polycrystalline silver at different concentrations of the indifferent electrolyte coincide within the experimental error limits, considering that the range of variation of the concentration only was half an order of magnitude.

Thus, in the case of electrodes with sharply different zero-charge potentials of the individual faces, the CTP for anion discharge should not coincide, since the structure of the electric double layer is not described by Grahame's theory, and studies at the individual single-crystal faces must be performed in order to establish the dependence of reaction rate on the metal type.

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COHERENT-OPTICAL STUDY OF THE MORPHOLOGY, SPECIAL STRUCTURAL FEATURES, AND MICRORELIEF ANISOTROPY OF POLYCRYSTALLINE ELECTROLYTIC DEPOSITS

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UDC 541.13:621.357

The paper examines the possibility of using Fraunhofer diffraction patterns (FDP) obtained from images of the surfaces of electrolytic deposits for a quantitative description of their structure and for a demonstration of special textural features hidden to the eye. It is shown for electrolytic copper deposits plated from $\text{CuSO}_4 + \text{H}_2\text{SO}_4$ solutions onto a mechanically polished copper substrate that by analysis of the FDP one can distinguish structural anisotropies due to mutual orientation of the crystals, to the arrangement of crystals in chains, and to the presence of slip bands, and one also can detect the characteristic confinement of crystals and blocks that cannot be discerned visually.

The basic information about surface texture and structure of electrolytic deposits usually is obtained by visual analysis of data obtained with light and electron microscopes. The information that can be extracted from photographs is vast, and provides an idea as to the special morphological features, and about the presence, mutual disposition and constitutional details of particular structural elements and defects. However, basically the information is descriptive in character, and the extraction of numerical surface parameters is restricted to the possibility of finding the average size and density of certain structural components (grains, pores, dislocations, etc.). This clearly is inadequate for an unambiguous quantitative description of the surface, and hence for theories of the formation of polycrystalline deposits.

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Translated from *Élektrokhiimiya*, Vol. 17, No. 4, pp. 569-575, April, 1981. Original article submitted April 18, 1980.