ELECTRODEPOSITION: DISCUSSION

The Nonuniformity of the Surface of the Electrode and the Mechanism of the Electrodeposition of Metals by A. T. Vagramyan

Yu. V. Lyzlov. A. T. Vagramyan indicated that heterogeneities of the cathode surface are formed because of the adsorption of foreign elements on different faces of the crystal of the electrodeposited metal. However, the separation of the surface into active and passive areas is not limited to separate faces of crystals: considerable areas of the cathode may be in very different states. We observed this phenomenon during the deposition of copper from a sulfate solution containing gelatin. The active areas had the shape of brilliant convex strips, and the areas between strips were covered with a thin matte precipitate. Investigation of this phenomenon allowed us to discover a series of interesting particularities of the process.* It was determined that the active state on the surface of the cathode is preserved if the current density at this surface exceeds a certain critical value. If the current passing through the cathode is insufficient to ensure this critical current density on the cathode, the surface becomes differentiated into active and passive areas. The metal is deposited mainly on the active surface areas. The dimensions of these areas accommodate themselves to the intensity of current in such a way as to favor the creation of the critical current density. If the current density in the circuit is changed, the area of the active region changes correspondingly. This phenomenon is registered on the polarization curves in that the cathode potential within a given interval becomes independent of the current passing through the cell. The active surface preserves a mirror finish independently of the duration of electrolysis. It is probable that this is the result of the specific mechanism of the process of deposition of the metal, which has a periodic character (the deposits have a layered structure). The passive areas have a matte finish. The electron-microscope photograph shows that in this case the deposit is formed of separate rounded blocks. One can imagine that they are formed in places where the adsorption layers blocking the passive surface are ruptured and then healed over again. These blocks are the cause of light scattering by passive surfaces.

A. N. Frumkin. I cannot agree with the argument presented by A. T. Vagramyan concerning the impossibility of applying the theory of retarded discharge to the discharge of metal cations. According to Vagramyan, the factors which retard the discharge during the process of electrodeposition should act in the reverse direction on the process of anodic dissolution, while the experiment shows the retardation of both processes. However, such reasoning is not correct. Regardless of the stage with which we associate a retardation of the process as a whole, if the whole thing is thought through and has no internal contradictions it must be applicable in an equal degree to the direct as well as the reverse process as long as we are close to the equilibrium potential. This conclusion in the most general form is drawn from the principle of microreversibility. Thus, if some intermediate stage of the process of discharge of hydrated cations becomes disadvantageous in terms of energy (due to the absorption of energy induced by dehydration) this disadvantageous stage inhibits to an equal degree the anodic process of transformation of metal atoms into ions. Unfortunately, the electrochemists often do not take into account the principle of microreversibility. These considerations become invalid for large deviations from the equilibrium potential.

A. T. Vagramyan—Answer to A. N. Frumkin:

The theory of retarded discharge takes into account the energy of the passage of ions from the solution to the surface of the metal. This passage is clearly indicated on the potential curves of ions and adsorbed hydrogen atoms. Both curves have minima corresponding to the equilibrium state: in the first case the minimum corresponds to the energy of ions in the solution, and in the second case to the energy of adsorbed atoms on the surface

---

*This work was done in the laboratory of A. G. Samartsev.

of the electrode. The potential curves indicate that the activation energies are not the same in the direct and reverse processes, since the energy levels (position of minima) are different. Consequently, it follows according to the theory of retarded discharge that the activation energy for the direct and reverse processes must be the same when the process occurs with high overvoltage, as was noted by A. N. Frumkin.

L. I. Antropov. According to A. T. Vagramyan, it should follow from the theory of retarded discharge that a considerable overvoltage can occur only during the cathodic deposition of metals while their anodic dissolution must occur without particular retardation and is not accompanied by overvoltage. The basis of this reasoning is that in the discharge of ions an expenditure of energy is necessary for their dehydration, while in the ionization of metals, on the contrary, there must occur a certain gain of energy due to the formation of a hydrated envelope. We cannot agree with this interpretation of the theory of retarded discharge. A. T. Vagramyan does not take into account the binding between the metal ion and the lattice of which it is a part. In our investigation we must take into account the binding energy in the anodic as well as the cathodic process. If we calculate the amount of hydration energy, H, and the binding energy of the metal ion with the metal lattice, U, then we obtain the following results for a series of metals having quite different overvoltages:

Ni^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}
586	403	528	355
472	535	460	371

A simple comparison of these figures indicates that the binding energy of the ion with the metal lattice is of the same order of magnitude as the binding energy of the ion with the solution (hydration energy). Consequently, according to the theory of retarded discharge, and contrary to what is proposed by A. T. Vagramyan, there is no basis for assuming a significant difference between the anodic and cathodic polarization of metals. At the same time these figures indicate that the theory of retarded discharge cannot explain the difference of overvoltage for different metals without taking into account some additional factors. In fact, if we compare the results obtained for nickel and zinc we find that for both cases the energies of hydration and the energies necessary to remove ions from the crystal lattices are very close. Furthermore, since H−U= kcal/ion-g for zinc and only 13 kcal/ion-g for nickel, one would expect a higher cathodic polarization during deposition of zinc than during deposition of nickel, although the experimental results are the reverse. Many investigators, among them A. T. Vagramyan, have noted previously that foreign particles present in the solution and capable of being adsorbed at the surface of the electrode have a considerable effect on the process of electrodeposition of metals. This description correctly reflects the experimental facts, but at the same time is much too general to serve as the basis for a definite statement concerning the direction of the effect these particles have on the value of overvoltage or a statement of the relationship between the overvoltage and the type of adsorbed particle, the nature of the metal, etc. Some of these questions can be investigated quite completely if one takes into account the null point of the metal. It is true that A. T. Vagramyan has indicated that the idea of the role of the null point in the electrodeposition of metals has been shown in the literature to be incorrect. He was referring to the following reference in his report to the preceding electrochemical conference: "During the deposition of silver from silver nitrate solutions the process occurs at potentials situated along the positive branch of the electrocapillary curve, i.e., the silver ions are discharged on the positively charged electrode; during this process no chemical polarization is observed although according to the theory of retarded discharge the presence of a strong repulsive field should induce a retardation of the electrochemical reaction. This contradicts the theory of retarded discharge and requires more precise study." [Transactions of the Electrochemistry Meeting (Izd. AN USSR, Moscow, 1953) p. 241] According to this interpretation it is really difficult to imagine why the discharge of silver ions occurs for practical purposes without overvoltage. However, in this case it is necessary to take into account that it is essentially anions which are adsorbed at the surface of the silver either under equilibrium conditions or when the current is applied ($\varphi_{Ag} = \epsilon_{Ag} - \epsilon_{Ag(q=0)} > 0$); the formation of an anion envelope must facilitate ionization and the discharge of the positively charged silver ions. Apparently such activating action of anions is characteristic not only for silver, but must exist in all cases when the surface of the metal is positive with respect to the solution ($\varphi_{Me} > 0$). This phenomenon was observed by Ya. M. Kolotyrkin during the deposition of hydrogen; to a considerable degree it must be the cause of low chemical polarization occurring during the deposition and dissolution of such metals as thallium, lead, cadmium, and some others.

During the deposition of metals whose potentials are more electronegative than their null points ($\varphi_{Me} < 0$) one would expect, on the contrary, adsorption not of anions but of cations, which may either be subject to discharge or incapable of discharging under given conditions. Nickel is among such metals. In the absence of an external current, the positively charged nickel ions, hydrogen ions, and ammonia and sodium ions in most nickel-plating baths will be attracted to the surface of the nickel electrode. When the cathode current is applied and the potential reaches the value at which the discharge and deposition of nickel ions becomes possible, the nickel ions would leave the double layer, while other cations which did not participate in the discharge would remain on the surface of the cathode. The replenishment of nickel ions in the double layer and their discharge will be continuously inhibited by the envelope of foreign cations. The degree of retardation,* and consequently, the magnitude of nickel deposition overvoltage, will depend on the volume concentration of foreign ions, their capacity of being adsorbed, their size, etc. One would expect, therefore, a change of overvoltage during the deposition of nickel when the concentration of foreign cations, and particularly H^+ ions, changes. When the concentration of H^+ ions decreases (obviously within certain limits), one must expect their retarding effect to decrease, and thus the overvoltage to decrease. Such a relationship has been determined by Z. A. Solov'eva and O. A. Abrarov in an investigation of cathodic deposition of cobalt and nickel. They found that for given values of pH a further decrease of acidity leads to a drastic decrease of cathodic overvoltage. Due to the fact that the null points for cobalt and nickel are quite different from each other and that the change of the value of overvoltage occurs in a narrow range of pH values, these authors assume that the null point potential plays no role in electrodeposition of these metals. They do not take into account, however, that under the conditions of their experiments both metals have a negative surface charge at potentials corresponding to the upper branch of the curve $\eta_{Me} = (pH)$ ($\varphi_{Me} = \epsilon_{Me} - \epsilon_{q=0} < 0$). Furthermore, if we take into account the distribution of the current between the reactions of the deposition of nickel and hydrogen (these authors do not do this, although they do give results concerning the current efficiency) the curve η_{Me} as a function of pH will be quite smooth. It must be noted that the decrease of overvoltage with increasing pH values was observed earlier also in the cathodic deposition of zinc, whose surface charge is also negative with respect to the solution.

Thus if one takes into account the null point or, more precisely, the potential of the metal, one can derive a much more detailed conception of the role of the composition of the solution and the nature of the metal on the creation of overvoltage.

One must not assume, and I am far from doing it, that all the multiple phenomena occurring during electrodeposition of metals can be explained only by the adsorption of cations and anions, and that the whole complex process of the formation of a new phase on the cathode can be reduced to the difference between the stationary potential of the metal and its null point. It is quite obvious that there exist other factors which play important roles in the process of deposition and dissolution of metals; most of them are taken into account by the modern theory of electrodeposition. Among these factors are the formation of the surface oxide, adsorption of uncharged particles, particularly atomic hydrogen, adsorption of organic molecules, hydrated oxides and basic salts of the deposited metal, change of the composition of the discharging ions, etc.

Z. A. Solov'eva and O. A. Abrarov, in their previously mentioned work, negate the role of the adsorbed hydrogen on the phenomena of electrodeposition of metals on the basis that they have not observed a direct parallelism between the current efficiency of hydrogen and the value of overvoltage of the metal. Furthermore, they observed a high polarization during the deposition of cobalt, when, in their opinion, all the current was used for the discharge of cobalt ions. However, one must keep in mind that the fraction of the current used for the deposition of hydrogen is not determined directly by the amount of hydrogen adsorbed at the surface of the metal. This depends first of all on the nature and potential of the electrode. It is well known that cobalt and nickel have high adsorption capacities with respect to hydrogen. It can be shown by calculations based on the results of the measurement of polarization that at potentials which, according to Z. A. Solov'eva and O. A. Abrarov, correspond to a 100% deposition of cobalt, there is quite a considerable fraction of the current (several tenths of a per cent) used in the discharge of H^+ ions. This amount of hydrogen is sufficient for the formation and preservation of the surface film which inhibits the discharge of cobalt ions. This effect of anions and cations is superimposed on the retarding effect of adsorbed hydrogen, and leads to a corresponding change of the electrode potential.

To conclude, the difference between my views and those of A. T. Vagramyan concerning the nature of electrodeposition of metals lies in the fact that while I accept the significance of passivating crystallochemical and hydrodynamic factors I also assume that the charge of the electrode, the phenomena of retarded discharge of ions, and the effect of adsorption of hydrogen play definite roles, while A. T. Vagramyan believes these latter factors play no role in the process of electrodeposition of metals.

DISCUSSION

A. T. Vagramyan—Answer to L. I. Antropov:

It seems quite strange that according to the theory of "null points" the negatively charged surface of electrodes inhibits the discharge of positive ions, since according to this assumption the foreign positive ions attracted from the solution to the surface of the metal do not participate directly in the electrochemical reaction, while ions which are regenerated at the electrode are almost unattracted and do not pass into the outer envelope of the double electric layer. Such an assumption seems illogical insofar as in the final analysis it is just these ions which are reduced at the surface of the electrode which pass through the double electric layer. L. I. Antropov does not explain why the ions not participating in the electrochemical reaction are adsorbed at the negatively charged surface while ions which are directly regenerated on the electrode are not adsorbed.

In this connection let us also consider the process of electrodeposition of silver, whose mechanism has been very well studied. It is well known that during the deposition of silver from nitrate solutions, the process proceeds at a potential considerably more electropositive than the null point (0.05 v). During the reduction of silver ions the process should be considerably inhibited because the positively charged ions are regenerated on the positively charged surface of the electrode. According to this theory, the fact that the charge is not retarded is explained by the adsorption of anions which facilitate the regeneration of silver ions. Also according to this theory, the "crystalline factors" have much less effect because of the adsorption of anions which increase the rate of the discharge of silver ions. However, it is well known that during the deposition of silver the crystal growth proceeds normally and the distribution of current on the surface of the crystal follows the basic laws of crystallography. It must also be noted that the crystals grow by layers whose thickness sometimes reaches a few thousands of atomic layers. According to the theory of L. I. Antropov it is not understandable how the anions adsorbed on the faces of the crystals can increase the rate of discharge if they are at a distance of a few thousands of atomic layers. And it must be noted that this theory, unfortunately, is not based on any experimental facts.

Certain Regularities of Electrocrystallization of Metals under the Influence of Alternating Current by A. A. Sutyagina and K. M. Gorbunova.

B. Ya. Kaznachev. The problem concerning the charge of the substances introduced or formed after their introduction can be solved definitely by studying the electrodeposition of metals under the effect of alternating current (A. A. Sutyagina, K. M. Gorbunova). In my opinion these authors have noted correctly that the coarsening of the structure and disappearance of brightness, if it occurs, can be explained by partial desorptions of positively charged foreign particles from the surface of the sample when it is made the anode. Nevertheless, there are substances of the anion type among the many brightness-inducing elements used in nickel plating. Apparently it is always necessary to consider the possibility that the additional element introduced into the electrolyte can, as the result of electrochemical reaction, form positively charged products of the colloidal type, which may strongly affect the cathode process. In connection with this, the investigation made by A. I. Bodnevas and Yu. Yu. Matulis (see p. 000) concerning the new electrolyte for bright tinning, is interesting. These authors express the opinion that the additional elements are reduced at the cathode and the products of this reaction act directly as brightness-inducing agents.

It must be noted that as a rule the investigators concerned with obtaining bright deposits give little attention to the electrochemical behavior of the organic element introduced into the bath. To a great extent this can be explained by the fact that organic electrochemistry is concerned very little with those substances which are used to brighten electrolytic deposits. This in turn is due to the fact that electrochemical reduction or oxidation of these substances proceeds simultaneously in different directions, and, mainly, to the fact that the current efficiency for such reactions is often very low. As a matter of fact it cannot be otherwise. If it were not so, the additional elements would be used up very fast. In the work done at the Division of Physical Chemistry of Chernovits University, a work at present being prepared for publication, an attempt is being made to explain the processes of formation of bright nickel deposits in baths containing some additional elements, namely the electrochemical and chemical reactions in the process of electrolysis which involve the additional elements.

One hopes that the investigation of the electrochemical behavior of different brightness-inducing agents will bring new and valuable results for the solution of the problem of obtaining bright deposits of metals on the cathode.

A. M. Ozerov. In 1955 we investigated the process of electrodeposition of nickel from an electrolyte containing 350 g/liter of $NiSO_4 \cdot 7H_2O$ + 10 g/liter H_2SO_4, using alternating current with an "anodic" component;

we showed that under these conditions the cathodic deposit has a high quality and is almost free of pores. We also investigated the effect of asymmetric alternating current on the structure of cathodic deposits of copper, nickel, and cadmium. The asymmetric alternating current was produced by superimposing a discontinuous symmetrical current on a direct current. When the ratio of the density of alternating to direct current was equal to 2, i.e., $i_{alt}/i_{dir} = 2$, and the rotation rate of the current interrupter was 60 and 2 rpm, we obtained an asymmetric alternating current with periods of T = 1 sec and T = 30 sec, and T_{dir}/T_{alt} = 0.5, 1.7, 4.1, 8.9, 18.5, 37.7, 76.1, and 152.9 for each period.

Using these different characteristics of asymmetrical alternating current, we studied the current efficiency, structure of cathodic precipitates, variation of cathode potential during electrolysis, and drew polarization curves by the ordinary compensation method and the method of rapid variation, worked out by A. T. Vagramyan (the reference electrode being saturated calomel). The polarization curves are represented in Figs. 1 and 2. These figures show that the polarization of the electrode by asymmetric alternating current makes the potential more noble. The main degree of ennoblement of the electrode potential occurred up to $T_{dir}/T_{alt} = 1.7$; as this ratio is increased the potential remains almost constant. Polarization of the electrode by asymmetric current leads to the periodic oscillation of the electrode potential between high values and very low values (Fig. 3).

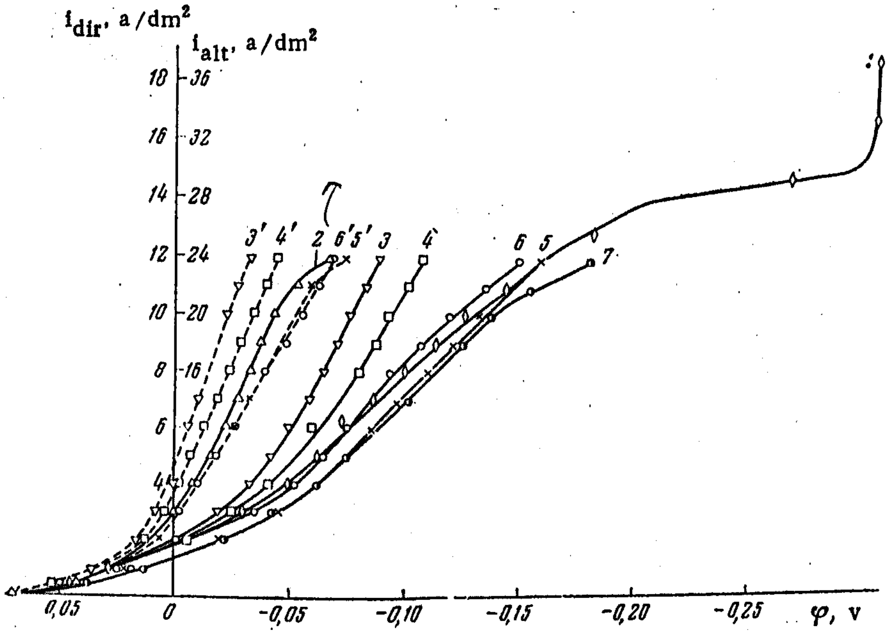


Fig. 1. Polarization curves obtained by the compensation method in a solution containing 200 g/liter $CuSO_4 \cdot 5H_2O$ + 50 g/liter H_2SO_4. Temperature, 30 deg C; $i_{alt}/i_{dir} = 2$. 1) Direct current; 2) T = 0; 3) T = 30 sec; $T_{dir}/T_{alt} = 0.5$; 4) T = 30 sec; $T_{dir}/T_{alt} = 1.7$; 5) T = 30 sec; $T_{dir}/T_{alt} = 4.1$; 6) T = 30 sec; $T_{dir}/T_{alt} = 8.9$; 7) T = 30 sec; $T_{dir}/T_{alt} = 18.5$. Curves 3' and 6' were obtained at the moment of application of alternating current.

Under the effect of polarization of the electrode by direct current alone the cathodic deposits are spongy, coarse, and bumpy (Fig. 4a) while the polarization of the electrode by asymmetric alternating current, even when the period of application of current is very short ($T_{dir}/T_{alt} = 153$), results in a considerable increase in the quality of the cathodic deposit (Fig. 4b). We found that the best cathodic deposits of copper are obtained when $T_{dir}/T_{alt} = 1.7$, and those of nickel when $T_{dir}/T_{alt} = 4$. When an alternating current is continuously superimposed on the direct current (T = 0) the cathodic deposits of copper are loose, highly dispersional, and dark red. Asymmetric alternating current has no great effect on the structure of cadmium deposits.

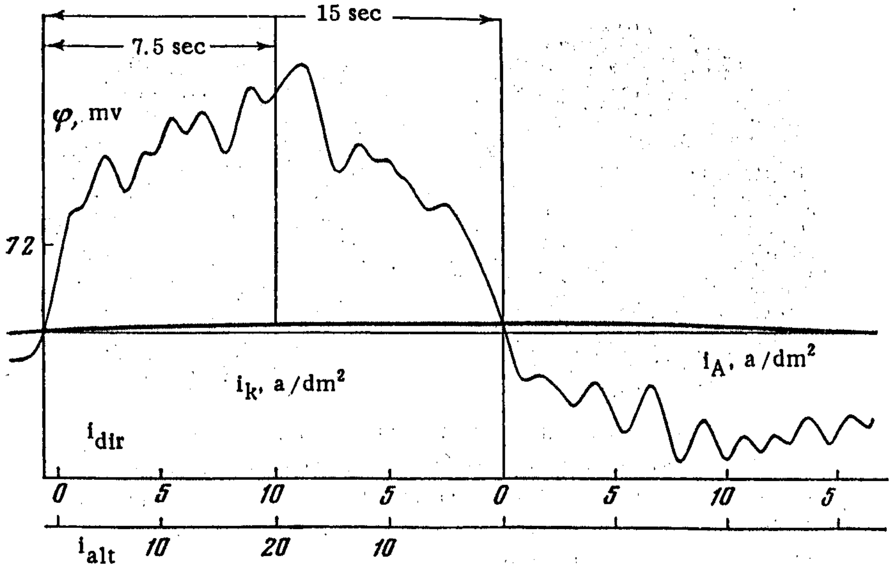


Fig. 2. Polarization curve obtained with rapid alternation. Temperature 30° C asymmetric alternating current; T = 1 sec; i_{dir}/i_{alt} = 1.7. Electrolyte: 200 g/liter $CuSO_4 \cdot 5H_2O$ + 50 g/liter H_2SO_4.

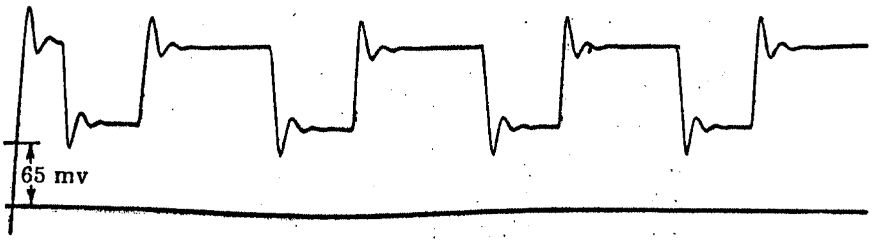


Fig. 3. Variation of the cathode potential as a function of time (120 sec). Temperature, 30° C ; asymmetric alternating current; T = 30 sec; T_{dir}/T_{alt} = 1.7; i_{dir} = 5 amp/dm²; i_{alt} = 10 amp/dm². Electrolyte: 200 g/liter $CuSO_4 \cdot 5H_2O$ + 50 g/liter H_2SO_4.

Results concerning the current efficiency and the porosity of nickel deposits are summarized in the table.

When the electrode is polarized by an asymmetric alternating current the electrode receives 50 "impulses" of current per second (the current density is tripled) under the effect of the "anodic" component of the current from the moment a 50-cycle alternating current is superimposed on the direct current. During the period betwe successive applications of alternating current the electrode is polarized by direct current alone.

It is well known that during the process of electrodeposition, the metal is deposited first of all on active areas, determined by the microgeometry and crystallographic particularities of the surface, and also by the presence of all kinds of adsorptional layers. During the "impulse" of the current a potential is reached at which the metal also begins to deposit on less active or inactive areas of the surface. The number of crystal nuclei and, correspondingly the rate of spread of the deposit in the direction of crystal growth, increases with the increase of current density. During the short period of time the electrode is under the influence of the "anodic" component of the current the areas of overvoltage of the surface are eliminated, and as a consequence the surface becomes filled with homogeneous crystalline planes.

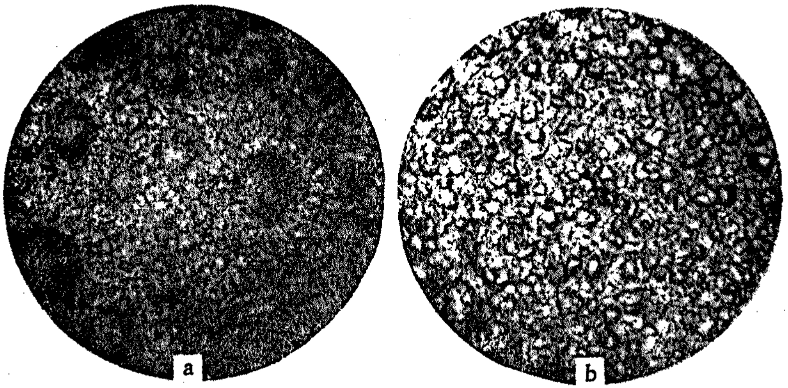


Fig. 4. Effect of alternating current on the structure of the copper deposit. a) Surface of the copper deposit (105x) obtained during 1 hr with i_{dir} = 8 amp/dm^2. b) Surface of the copper deposit (105x) obtained during 1 hr with T = 30 sec; T_{dir}/T_{alt} = 153.5; i_{dir} = 8 amp/dm^2; i_{alt} = 16 amp/dm^2.

Current Efficiency (A, %) and Porosity of Nickel Deposits (pores/cm^2) Obtained in the Electrolyte: 350 g/liter $NiSO_4 \cdot 7H_2O$ + 30 g/liter H_3BO_3, at 30 deg C; i_{dir} = 5 amp/dm^2; i_{alt} = 10 amp/dm^2; duration of electrolysis, 30 min.

T_{dir}/T_{alt}	T = 30 sec		T = 1 sec	
	A, %	pores/cm^2	A, %	pores/cm^2
0,5	84,00	2	91,04	0
1,7	88,35	2	91,47	1
4,1	91,78	0	94,00	1
8,9	92,60	1	92,44	1
18,5	93,36	2	91,70	2
37,7	93,44	7	94,06	2
76,1	94,91	5	94,11	2
152,9	—	6	—	2
Direct current	95,00	27	94,93	26

Yu. Ya. Vene and S. A. Nikolaeva [Zhur. Fiz. Khim. 29, 811 (1955)] have shown that when the direction of current is periodically alternated during electrodeposition of copper, aside from the elimination of irregularities from the electrode surface and the corresponding decrease of concentration polarization, the state of the surface is altered, which in a surface bath is possibly nothing else but passivation. The results obtained by these authors concerning anodic polarization lead us to assume that during the short period of time that the electrode is under the influence of the "anodic" component of the current a more stable adsorptional layer is formed on the most active areas of the surface. This adsorptional layer leads to the leveling of the activity of different areas of the surface and to the formation of compact cathodic deposits during subsequent electrodeposition.

Thus a periodic combination of the impulses of current of the "anodic" component of the current and the subsequent ordinary processes of electrodeposition (during direct current) favors the formation of dense deposits with a more homogeneous surface and fewer porosities.

The considerable ennoblement of the electrode potential, during the polarization of the electrode by asymmetric alternating current when the ratio T_{alt}/T_{dir} is small or when T = 0 is apparently due to the changes occurring in the composition of the preelectrodic layer of the solution. The formation of loose, dark-red deposits of copper with continuous application of alternating current (T = 0) and when the ratios T_{alt}/T_{dir} ($i_{alt}/i_{dir} > 1$) are small is in good agreement with the conclusion arrived at earlier by K. M. Gorbunova and A. A. Sutyagina [Zhur. Fiz. Khim. 3, 542 (1955)]. Under these conditions considerable numbers of Cu^+ ions are accumulated in the preelectrodic layer, creating favorable conditions for the reaction: $2Cu^+ \rightarrow Cu + Cu^{2+}$. The highly dispersional copper which is deposited under these conditions hinders the normal growth rate of the crystals and the result is loose, dark-red cathodic deposits.

The decreased porosity of nickel deposits during polarization of the electrode by asymmetric alternating current is due to the favorable conditions of electrodeposition indicated above, which occur as the result of the decrease of adsorption of nickel hydroxide or its basic salts at the cathode; (this is in agreement with the conclusions reached by A. T. Vagramyan).

The Neutralization of Metallic Ions at Macrodistances from the Cathode by V. A. Yurkov

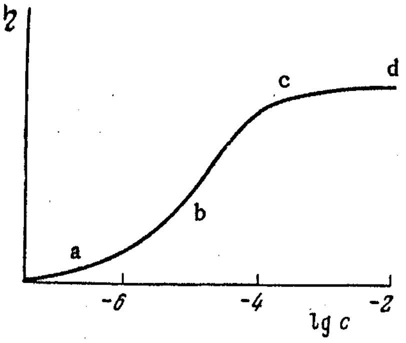
Yu. V. Baimakov. Briefly, I would like to note that it is difficult to accept V. A. Yurkov's assumption that the mean free path of electrons is so large in the solution in which there are colossal numbers of ions and molecules of water. The electrons cannot pass beyond the double electric layer. Therefore one must look for another cause of the appearance of a dispersional layer of copper at a considerable distance from the cathode.

N. T. Kudryavtsev. The opinion of V. A. Yurkov derived from his experiments that the ions are neutralized at macrodistances from the cathode is incorrect and it is difficult to understand the origin of this opinion. Since in his case the electrolyte was KNO_3 or $NaNO_3$, the copper was dissolved at the anode, with subsequent deposition of colloidal copper hydroxide as the result of hydrolysis, while ammonia, resulting from the reduction of NO_3^-, was deposited on the cathode.

B. S. Krasikov. During recent years considerable numbers of investigations have appeared which are concerned with the effect of surface-active substances on processes of electrodeposition of metals. It must be noted that, unfortunately, it is very difficult to compare and reproduce these results. In my opinion this situation is the result of the fact that very often in these investigations there are no indications concerning the character of adsorptional layers or the concentration of surface-active materials; (usually the investigators limit themselves to the indication that the solution is saturated by the addition of these elements or is diluted *n* times).

If we study the variation of overvoltage (when i = constant) at different concentrations of additional elements, we obtain a curve of the type shown in the figure. This type of curve corresponds to a more or less homogeneous electrode surface. If the surface of the electrode is not homogeneous, i.e., the activity of various areas of the surface are considerably different, the curve representing the variation of the ion-discharge overvoltage as a function of the concentration of surface-active substances shows breaks. Within the range of concentration of these surface-active substances indicated by A-B on the curve, the discharge follows very closely the equation derived on the theory of retarded discharge, which takes into account the effect of diffusion. However, the rate of the process at high concentrations of surface-active substances, when the concentration is close to saturation, i.e., section C-D on the curve, becomes different; it is related essentially to the difficulty of the discharging ions in reaching the surface of the electrode, and to the penetration of ions through the layer. Therefore when there are no indications as to the range of concentrations within which the measurements were made, it becomes very difficult to interpret and compare the experimental results.

Usually the authors limit themselves to a purely qualitative interpretation of the phenomenon, yet it seems to me that in a number of cases it would be possible to treat the results semiquantitatively and sometimes quantitatively. If one uses the equation taking into account the simultaneous effect of the retarded diffusion and discharge, which includes the term which takes into account the variation of overvoltage due to sepcific adsorption, and if in the total shift of the potential, one accounts for the part which is determined by the retardation of each of the stages (diffusion and discharge), one can determine quantitatively the rate of discharge at a given concentration of the surface-active substance. It is well known that the presence of surface-active substances adsorbed on the surface of the electrode does not affect the diffusion rate, while the rate of discharge depends considerably on the adsorption potential; (in a number of cases the shift of overvoltage reaches 0.6-0.8 v). As the role of the concentration polarization increases, the effect of surface-active substances on the rate of ion discharge decreases.



Variation of the electrodeposition overvoltage as a function of the logarithm of the concentration of the surface-active substance.

One can calculate the part in the total effect of retardation due to the retardation of discharge and that part due to the diffusional processes. This is easy to do if one takes the ratio of the current densities at a given potential but at temperatures differing by 10 deg. If $i_{t+10}/i_t = 2$ then the retardation is due to the discharge; if $i_{t+10}/i_t = 1.2$ then the total retardation of the discharge is determined only by the retardation of the diffusion; when the value of the numerical temperature coefficient is between 2 and 1.2, one can calculate the part (in other words, the kinetic portion) of each stage of the total effect of the retardation process. These calculations are possible if one knows precisely the limits of the concentration within which the experiment was performed -- at relatively low concentrations (section A-B), or high concentrations (C-D) -- since in these limit cases the effects are quite different. Our reasoning refers to a relatively small portion of the surface covered by the adsorbed substance; however, analogous calculations can be made also when a considerable area of the surface is covered if one knows the relationship between the limit current and the concentration of the surface-active substance, or, what is the same thing, the relationship $i = f(\theta)$, where θ is the area of the surface covered.

Mechanism of Electrolytic Deposition of Metals on Passivated Surfaces by L. I. Kadaner and A. Kh. Masik

B. Ya. Kaznachei. A few works concerning the report by L. I. Kadaner:

1. In our investigation concerning the electrodeposition of permanently magnetic alloys we used separating layers for the analysis of the alloys. The alloys were deposited on the "separating layer," which was then removed from the base, and this procedure considerably facilitated the analysis of the alloys. Furthermore this method allowed us to check the porosity of the electrodeposited layers of metals; the metal layer deposited on the separating layer was removed and examined under the microscope, the layer being lighted from the back side. The degree of porosity can also be conveniently investigated by depositing the metal on a conducting layer deposited on a transparent insulator; one can count the number of pores, observe their dimensions, shape, and location.

2. An opinion was expressed that it is impossible to plate rotating cathodes with chromium. I would like to point out the practice in the printing shop of the newspaper "Pravda," where printing rollers of large diameter and length are chromium-plated by putting the rotating cathode in a horizontal position in the electrolytic bath, the cathode being partially immersed. The rotation rate of the cathode is regulated to keep the roller constantly under a layer of the electrolyte. This principle was used for the electrodeposition of magnetic alloys. When the drum cannot be immersed in the bath the alloy can be deposited with the drum rotating just at the surface of the electrolyte.

3. Experiments showed that copper deposits with a fine crystal structure are very hard and withstand bending 10-12 times; deposits with a coarser structure withstand bending 2-3 times. Experiments with copper dies with different structures subjected to pressure show that the harder the copper the higher the resistance of the die; dies with a fine crystal structure do not show the defect known as "pressing through." In this defect the pattern of the structure of the metal under high pressure in the press is transferred to the face side of the die and is imprinted on the plastic material being formed. Therefore when dies are prepared by electrodeposition it is very important to obtain deposits of hard copper, which have a fine crystal structure.

N. T. Kudryavtsev. The assertion by L. I. Kadaner and A. Kh. Masik concerning the necessity of passivating the cathode to ensure solid binding between the coating and the base metal needs clarification. I agree that in some cases preliminary passivation of the surface of the cathode increases the strength of the binding (for example, when nickel is deposited on steel after surface treatment in concentrated sulfuric acid). However, I believe that the cause of the favorable effect of such a treatment is not the presence of the passivating film on the surface, but the fact that the passivating film is formed after the entire surface becomes completely clean and homogeneous as the result of the treatment. It is important that such a surface state be preserved up to the moment of cathodic polarization during electrodeposition of the metal, when the surface is again liberated from the oxide film and becomes active.