NUCLEATION OF SILVER
ON PLATINUM ELECTRODE
UNDER GALVANOSTATIC CONDITIONS*

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Dedicated to the 65th anniversary of the late Academician R. Brdička.

An equation of the galvanostatic η–t curve for nucleation of metals on an inert electrode was derived. It was verified by employing galvanostatic pulses with potentiostatic control of the electrode potential before and after the pulse. The measured η–t curves are in accord with calculated ones. The dependence of crystal growth on overvoltage after the pulse was explained in terms of a two-dimensional nucleation at an overvoltage exceeding 8 mV. The supersaturation during nucleation was 12—18, critical overvoltage 40—90 mV and the activation energy of the formation of nuclei $4 \cdot 1 \cdot 10^{-14}$ erg. The behaviour of the system under study is an evidence for participation of the electrode material during nucleation.

The equation of the galvanostatic η–t curve for heterogeneous nucleation in electro-crystallization of a metal on a different metal electrode was first derived by Gucov[1] in the form

$$\eta = (RT/zF) \ln (1 + it/zFc_0).$$ (1)

Since he did not consider the charge transfer overvoltage his equation gives smaller η values than those which are found experimentally.

THEORETICAL

We shall consider an inert electrode dipped in a solution of metal ions. After the current is switched on and the electrode double layer is charged, discharged adatoms are accumulated on the electrode until nuclei of the deposited metal are formed[5]. The current is given by the equation of transfer reaction in which the anodic part of the current is corrected for the concentration of adatoms[2]. This concentration and the total overvoltage are functions of time:

$$i - C_{DL}\, dn/dt = i_0\{[c(t)/c_0]\exp\left[\alpha zF\eta(t)/RT\right] - \exp\left[(\alpha - 1)\, zF\eta(t)/RT\right]\}\,. \quad (2)$$

The second term on the left side describes the charging of the capacity of the electrode double layer. This capacity is, however, by several orders of magnitude smaller than that due to adatoms on the electrode[3], so that it can be neglected.

The time dependence of the concentration of adatoms is given by the equation

$$c(t) = it/zF + c_0\,. \quad (3)$$

Introducing Eq. (3) into (2) we obtain an implicit function for the overvoltage at time t

$$i/i_0 = \exp\left(\alpha zF\eta_t/RT\right) + (it/zFc_0)\exp\left(\alpha zF\eta_t/RT\right) - \exp\left[(\alpha - 1)\, zF\eta_t/RT\right] \quad (4)$$

which cannot be solved with respect to η_t but t can be separated — an advantage in calculating the course of the curve:

$$t = (c_0 zF/i)\left[\exp\left(- zF\eta_t/RT\right) - 1\right] + (c_0 zF/i_0)\exp\left(- \alpha zF\eta_t/RT\right)\,. \quad (5)$$

The exponential terms in Eq. (4) can be expanded in series. For time intervals longer than necessary to charge the double layer but shorter than the time of formation of a nucleus, i.e. $RTC_{DL}/zFi_0 < t < \tau$, and for small overvoltages, $\eta_t \ll RT/zF$, the nonlinear terms can be neglected. Thus we arrive at the simplified expression

$$\eta_t = iRT(c_0 zF - i_0 t)/i_0 zF(c_0 zF + i\alpha t)\,. \quad (6)$$

At small currents, $i \leqq 10^{-3}$ A/dm^2, and with $c_0 \approx 10^{-10}$ mol/cm^2, $t \approx 10^{-3}$ s the second term in the denominator attains values by two orders of magnitude smaller than the first one and can therefore be neglected. We then obtain an equation of a straight line by which we approximate the course of the curve in the initial stage:

$$\eta_t = iRT/i_0 zF - iRTt/c_0 z^2 F^2\,. \quad (7)$$

At time $t = 0$ the second term on the right-hand side equals zero. From the first one, which is the product of current and polarization resistance, it is possible to calculate the exchange current density i_0. From the slope of the straight line, Eq. (7), the equilibrium concentration of adatoms, c_0, can be found.

To determine the supersaturation at the moment of formation of the nucleus, c_τ/c_0, Eq. (2) can be rearranged to

$$c_\tau/c_0 = (i/i_0)\exp\left(- \alpha zF\eta_t/RT\right) + \exp\left(- zF\eta_t/RT\right)\,. \quad (8)$$

For $i \ll i_0$ the first term on the right-hand side attains very small values and can be neglected. The second one can be formally derived from the Nernst equation for the crystallization overvoltage. However, this way to determine the supersaturation is not accurate enough[2]; it is better to start from the charge passed through the electrode during the time interval from $t = 0$ to $t = \tau$. We obtain from Eq. (3)

$$c_\tau / c_0 = i\tau / zFc_0 + 1 . \qquad (9)$$

The activation energy of formation of nuclei is determined from the rate of nucleation as in reference[5].

EXPERIMENTAL

The determination of the rate of nucleation is based on the Volmer ideal experiment[3] in which a defined supersaturation is formed in the given system for a certain time in order that nuclei can be formed. After their formation the experiment is interrupted, the nuclei are removed and counted. Naturally they cannot be counted immediately since they are too small. Therefore, in reality the experiment is not interrupted after the period of high supersaturation, but the super-saturation is lowered under the critical limit and the nuclei are allowed to grow up to a suitable size.
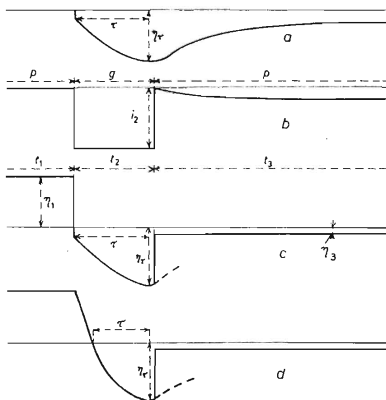

Fig. 1

The Course of Potential and Current During Nucleation

a Potential (theoretical); b current in the $p—g—p$ method; c potential in the $p—g—p$ method (theoretical); d potential in the $p—g—p$ method (experimental).

High supersaturation was attained in earlier work[4] by a potentiostatic pulse. Since, however, in this method the supersaturation is not constant as erroneously assumed, and its measurement is difficult[2], we used instead of it a galvanostatic pulse. Its length was chosen so that nuclei were just formed on the electrode. Afterwards the electrode potential was controlled potentiostatically and the nuclei were allowed to grow at a small overvoltage, hence at a small supersaturation and small crystallization overvoltage, until they were visible by a microscope. Since the measured values depend on the history of the electrode before the pulse[5], the electrode potential in that period was controlled also potentiostatically. We denote this method of measurement as *p-g-p*.

The theoretical course of the electrode potential during the galvanostatic pulse is shown in Fig. 1*a*. After switching on the current the potential jumps to a certain value from which it rises continuously to a maximum corresponding to the formation of nuclei. Then it decreases. In Figs 1*b* and 1*c* there are shown the theoretical courses of current and potential in the *p-g-p* method.

We used in the measurement a type 1210 potentiostat of the G. V. Akimov State Research Institute for Material Protection. Constant current was realized by a 240 V battery with a suitable series resistance. A polarized relay controlled by a pulse generator served to switch over from one source to the other. The course of the electrode potential during the galvanostatic pulse was observed and photographed on a Type K 564 oscilloscope (Křížík, Prague). A platinum wire 1 mm in diameter, sealed in glass and ground perpendicularly to its axis, served as electrode. The counter and reference electrodes were made of silver. The potential measured against the reference electrode was equal to the overvoltage.

The electrodes were placed in a vessel with a planparallel bottom through which the platinum electrode was observed by a metallographic microscope of the type MIM 6 at a 90 fold magnification.

The measured solution was 6M-AgNO₃ prepared from triply distilled water and doubly re-
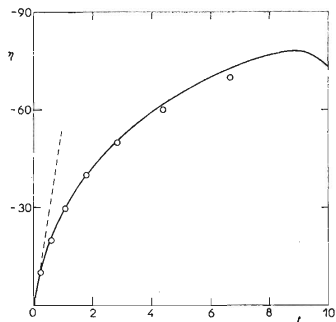

Fig. 2

Galvanostatic η–t Curve

Measured curve with calculated points; η in mV, t in ms.
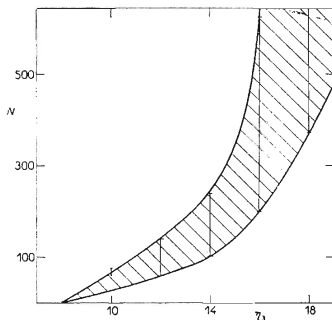
Fig. 3

Dependence of the Number of Grown Crystals per cm^2 on Overvoltage η_3 (mV)

crystallized nitrate. The solution was purified by a long preelectrolysis with a silver anode as described earlier[5]. Its preparation as well as the measurement proceeded in a purified argon atmosphere. The temperature was 25°C.

The method of measurement was as follows. The electrode was first maintained for 2 min at an overvoltage $\eta_1 = +50$ mV. Then the galvanostatic pulse was applied and afterwards the electrode was polarized at an overvoltage $\eta_3 = -5$ to -20 mV. The nuclei formed during the pulse grew during the last period to crystals which were counted.

RESULTS AND DISCUSSION

Galvanostatic Curve During Nucleation

The measured galvanostatic curves are similar to the theoretical ones except that they show no potential jump on changing the polarization from potentiostatic to galvanostatic; the potential rises continuously from positive to negative values (Fig. 1d). We shall discuss this phenomenon later.

At negative overvoltages, however, the curves were well developed and suitable to check Eq. (4) and (5). The curve obtained at $i_2 = 8\cdot4$ mA/cm² is shown in Fig. 2. For its calculation the equilibrium concentration of adatoms and exchange current density must be known. The former was calculated from the slope of the tangent in the point $t = 0$ with the use of Eq. (7). From the slope of 58 V/s we obtained $c_0 = 3\cdot8 \cdot 10^{-11}$ mol/cm².

The exchange current density cannot be calculated from the experimental curve since the initial potential jump is absent. This shows that either the exchange current density is very large resulting in a small jump which is masked by experimental errors, or there are other reasons. The standard exchange current density, i_0^0, for silver after Gerischer[6] is 24 A/cm²; an extraordinarily high value was assumed also in his other work[7].

The mentioned fact simplifies our calculations. With increasing i_0 the value of the second term on the right-hand side of Eq. (5) diminishes being only 1/100 of the first one at $i_0 \approx 10$ A/cm², so that it can be neglected. We then have

$$t = (c_0 z F/i) \left[\exp\left(-z\eta_t/RT \right) - 1 \right], \qquad (10)$$

where i_0 is not involved. The calculated points lie on the given curve (Fig. 2) showing a good agreement between measured and calculated values. The comparison was made also with several other curves with the same result; the derived equation describes the η–t curve very well.

Eq. (10) can be used also to calculate the equilibrium concentration of adatoms, c_0, after introducing the experimental η_t and t values. For $t = 0\cdot002$ s, $\eta_t = -43$ mV we obtain $c_0 = 3\cdot8 \cdot 10^{-11}$ mol/cm² in accord with the above-mentioned result.

The atomic radius of silver is 2.88 Å, hence $1.2 \cdot 10^{15}$ atoms/cm^2 or $2 \cdot 10^{-9}$ mol : : cm^2 is necessary to cover the surface with a monolayer. In our case the electrode surface is covered only to 1.9% of a monolayer.

The equilibrium concentration of adatoms is of the order of magnitude as found earlier[5] for nucleation of tin on platinum: $c_0 = 1.5 \cdot 10^{-11}$ mol/cm^2. Also the surface coverage with adatoms is close to the value of 0.73% for tin. Our results are in the range of the equilibrium concentration of adatoms during electrocrystallization of silver on a silver electrode after Bockris[8]: $(0.3 - 16) \times 10^{-10}$ mol/cm^2. Gucov[1] found a much higher value for the equilibrium concentration of cadmium adatoms on platinum than in our case: $c_0 = 1.5 \cdot 10^{-10}$ mol/cm^2; surface coverage $7 - 8\%$. The literature data are widely scattered owing to differences in the studied systems and to a poor reproducibility of results with different electrodes etc. From this point of view, our results are in a satisfactory agreement with the literature data.

We shall consider now the initial part of the galvanostatic curve at positive overvoltages. From the fact that the electrode potential rises continuously (not abruptly) after switching on the current it follows that an electrochemical process proceeds at the electrode. This is obviously deposition of silver at more positive potentials than the equilibrium one, since other reactions are excluded by the choice of experimental conditions. An analogous case is the deposition of copper on platinum[9] or the deposition of bismuth, cadmium etc. on silver and other metals[10]. Its explanation is based on a strong adsorption of the deposited atoms on the electrode. The activation energy of the transfer reaction is diminished by the adsorption energy, hence the deposition proceeds at a more positive potential. In addition, also the formation of intermetallic compounds can cause the same effect.

The deposition of silver at more positive potentials can be thus promoted in two ways until all sites on the electrode necessary for the mentioned reactions to proceed are blocked. No silver nuclei can then be formed, a fact which was proved by polarization of the electrode at $5 - 10$ mV (vs the equilibrium potential) for several hours. However, such sites on the electrode can probably promote the formation of nuclei at negative overvoltages.

Further we attempted to prove whether the maximum on the η–t curve corresponds to formation of nuclei. For $\eta_1 = +50$ mV, $i_2 = 7.95$ mA/cm^2 and $\eta_3 = -10$ mV we varied the length of the pulse so that it ended either before or behind or at the maximum on the curve; e.g. the maximum was at $\tau = 5.5$ ms and the pulse length 5.2, 5.5 and 5.8 ms. A current flows through the electrode during the period t_3 only when nuclei are formed. Their growth results in an increase of their surface, hence in an increase of the current.

For $t_2 < \tau$ no current flowed during the period t_3, but for $t_2 > \tau$ it did flow always. For $t_2 = \tau + 0.3$ ms the current increased slowly, but for larger t_2 rapidly. This is apparently in connexion with the mode of crystallization on the nuclei. For $t_2 = \tau$ the current in certain cases flowed, in other did not owing to a certain scattering of the τ value.

We conclude that the maximum on the curve corresponds to the formation of nuclei so that it can serve as an indication of their formation.

The occurrence of a maximum on the curve followed by a decrease of potential is sometimes attributed to a decrease of the concentration of adatoms during formation and growth of nuclei resulting in a decrease of the crystallization overvoltage. Another possible cause would be an increase of the active surface of the electrode resulting in a decrease of the current density. We shall evaluate both possibilities.

If the nucleus consisted of 100 atoms and if 10^5 nuclei/cm^2 were formed on the electrode, then 10^7 atoms would be consumed. The equilibrium concentration is $3 \cdot 8 \cdot 10^{-11}$ mol/cm^2 or $2 \cdot 3 \cdot 10^{13}$ atoms/cm^2. At a tenfold supersaturation the concentration of adatoms before nucleation would be $2 \cdot 3 \cdot 10^{14}$ atoms/cm^2. The consumption of 10^7 atoms in nucleation obviously cannot influence the concentration or the crystallization overvoltage. This conclusion would remain valid even if the number of atoms per nucleus, the supersaturation and the number of nuclei were by an order of magnitude higher. A local decrease of the number of adatoms is compensated by deposition of further metal atoms and also by diffusion from near enriched zones. The current of 1 mA causes deposition of $6 \cdot 10^{12}$ atoms in 1 ms, the mentioned decrease in the concentration of adatoms being thus compensated in 10^{-8} s.

The decrease of overvoltage after formation of nuclei could be caused also by a drop of current density as a result of increased active surface area of the electrode. This effect can be estimated directly from the polarization curve[2]; an increase in surface area can result in a drop of overvoltage by several tens of millivolts (Table I). Obviously this effect could play a role in the formation of the maximum. However, no attempt will be made to decide definitely between both mentioned effects.

TABLE I

Decrease of Overvoltage with Increasing Active Surface Area of Electrode

Increase of surface area	$i_{new}/i_{orig.}$	$\Delta\eta$, mV
1·5×	1/1·5	10—12
2×	1/2	17—20
5×	1/5	30—42
10×	1/10	50—58

The Growth of Nuclei

In determining the rate of nucleation from the number of grown crystals, we used originally the smallest possible overvoltage of several millivolts. Althoug the η–t curve on the oscilloscope during the galvanostatic pulse exerted a distinct maximum followed by a decrease in overvoltage,

so that nuclei were formed, no crystals grew on the electrode. The current was zero during the period t_3.

However, when the overvoltage η_3 was increased, a current began to flow during the period t_3 and crystals grew on the electrode. The critical limit of overvoltage was about 8 mV. This statement is in contrast to the work of Pangarov[11] who used an overvoltage of $5-7$ mV for the growth of silver nuclei formed during a potentiostatic pulse.

The reason for this is probably that in our experiments the nuclei had a more perfect structure. During a galvanostatic pulse the adatoms are accumulated on the electrode gradually and nuclei are formed from them relatively slowly. It is likely that the atoms tend to occupy the sites that correspond to a perfect lattice without defects or screw dislocations. Matthews[12] found indeed after a similar slow formation of silver nuclei (during vacuum evaporation) crystals of the size of 10^{-18} cm^3 which according to moiré stripes had a perfect lattice. In our case the experiment is interrupted after formation of nuclei and the conditions for a slow growth are realized. In view of the perfect structure of every nucleus, after filling one plane a two-dimensional nucleus of a further plane must be formed. For this process an overvoltage of $8-12$ mV was indicated by Budewski[13] in good agreement with our critical overvoltage value.

If the pulse is considerably prolonged or if the current density during the pulse is elevated by one or two orders of magnitude, no critical value of the overvoltage is observed and the nuclei grow even at small overvoltages. Their formation and growth is in both last cases very rapid already during the pulse so that screw dislocations may be formed enabling growth without two-dimensional nucleation. The
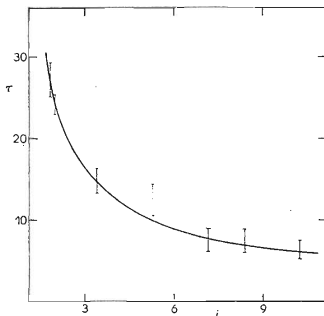

Fig. 4

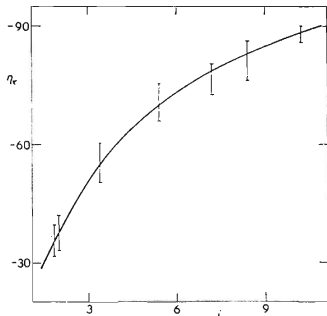Dependence of the Time of Nuclei Formation τ (ms) on Current Density i (mA/cm^2)

Fig. 5

Dependence of Critical Overvoltage η_τ (mV) on Current Density i (mA/cm^2)

mentioned Pangarov's finding can be explained analogously. In his case the over-voltage at which the nuclei were formed was considerable (hundreds of mV). The nuclei must have been formed very rapidly and grew probably further for a certain time at that overvoltage at an extremely high current density. Under such conditions many defects and dislocations were formed so that no two-dimensional nucleation was necessary for further growth. Our explanation is substantiated by the finding[14] that the deposition of silver on graphite proceeds by two-dimensional growth of crystals.

When we further increased the overvoltage η_3 we met an unexpected effect: the number of grown crystals, which should be according to the original concept equal to the number of nuclei, increased with increasing overvoltage being close to zero at 8 mV. At the same time the number of crystals showed an increasing scatter (Fig. 3).

It is difficult to explain this effect on the basis of the original concept. If the nuclei were formed only during the period t_2, their number could not be influenced by the conditions of the next period. Since they cannot be formed in the period t_3 we must assume that approximately the same number of nuclei is formed at constant conditions, but only some of them are selected for further growth, this selected fraction depending on the overvoltage. The conditions for the selection are apparently given by the structure of the nuclei and of the electrode in their proximity, besides over-voltage or suppersaturation. Also the fact that the nuclei are not formed at once but during a certain period, hence that the nuclei formed sooner grow for a certain
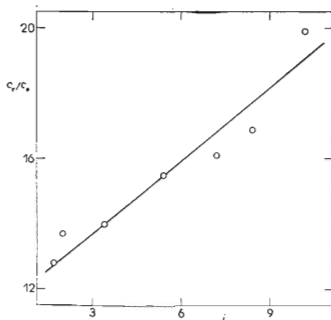

FIG. 6

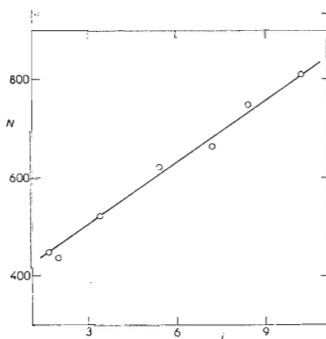Dependence of Supersaturation c_r/c_0 During Nucleation on Current Density i (mA/cm^2)

FIG. 7

Dependence of the Number of Grown Crystals per cm^2 on Current Density i (mA/cm^2)

time during the pulse (resulting in a "spectrum" of nuclei of different size after the pulse is finished) contributes to the scatter in the measurement as well as to the mentioned dependence. Its satisfactory explanation, however, requires a further study of all the mentioned factors.

Parameters of Nucleation

The critical time interval τ during which the nuclei are formed was determined from the galvanostatic curves and is shown in Fig. 4 as a strongly decreasing function of the current density. At higher current densities the time τ should approach a limiting value of about $6-8$ ms. An analogous quantity found in the nucleation of tin[5] is $10-15$ ms, hence roughly of the same order of magnitude. It can be assumed that this limiting time is in connexion with the proper rate of crystallization, *i.e.* the rate at which atoms are ordered in space to form a crystallographic lattice.

A similar but inverted form is observed in the dependence of the critical overvoltage at which the nuclei are formed on current density (Fig. 5). It should also attain a limiting value at higher current densities, namely about 120 mV. This value is different with different metals being about 18 mV with tin[5] and 30 mV with cadmium[1].

The dependence of the critical supersaturation, determined from the charge according to Eq. (9), on current density is linear and moderately increasing (Fig. 6). The values measured in the present work are higher than in nucleation of tin[5] $(2-3)$ and cadmium[1] $(3-8)$ on platinum. The dependence of the number of grown crystals on current density is analogous (Fig. 7) in accord with the mentioned increase in supersaturation.
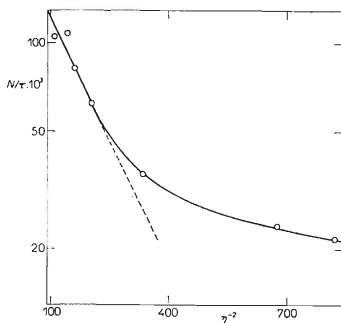

FIG. 8
Dependence of the Rate of Nucleation N/τ (cm^{-2} s^{-1}) on Overvoltage η^{-2} (V^{-2})

The activation energy of nucleation can be determined from the dependence of the nucleation rate on the reciprocal square of the critical overvoltage (Fig. 8), which should be linear. It is, however, linear in our case only in the region of high overvoltages owing apparently to an influence of the electrode material on nucleation. We assume that on the electrode there is a certain number of sites suitable for nucleation and differing from the energetical point of view. These sites will be utilized according to their preference with increasing overvoltage. The rate of nucleation will be initially determined by the number of preferred sites and by the overvoltage so that no linear dependence can be expected. However, when the critical overvoltage increases so that all preferred sites are occupied, the rate of nucleation will be determined only by the overvoltage. Therefore the linear dependence is observed only at higher overvoltages.

It follows from the slope of the linear part that $k_2 = 2 \cdot 63 . 10^{-16}$ erg V^2 whence at the mean critical overvoltage $\eta_\tau = -80$ mV the activation energy $A_k = 4 \cdot 1 .$ $. 10^{-14}$ erg or 590 cal/mol. This is very low, about by an order of magnitude lower than with tin[5] or other metals[1]. Similar values were indicated by Kaišev[4] for nucleation of silver on platinum: $(2 \cdot 9 - 6 \cdot 7) . 10^{-14}$ erg. From the activation energy the number of atoms in a nucleus can be determined as smaller than one in our case, which is of course absurd. The very low activation energy of nucleation together with the dependence of the process on overvoltage η_1 and η_3 and other results are an evidence for a considerable interaction between the electrode material and the forming nuclei.

The behaviour of the electrode differs in some cases from the model of nucleation on an inert metal proposed originally. To obtain a deeper insight in the process it will be necessary to take into account the relation between the crystals in the electrode and those of the deposited metal; the nucleation will then be understood as a special case related to epitaxial or isomorphous growth of two metals. This will be the subject of further work.

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