JOURNAL OF APPLIED ELECTROCHEMISTRY 8 (1978) 531–535

The mechanism of formation of a surface film of silver on a platinum electrode in galvanostatic deposition

K. I. POPOV, M. G. PAVLOVIĆ, M. D. MAKSIMOVIĆ

Faculty of Technology and Metallurgy, University of Beograd, Beograd, Yugoslavia

Received 9 January 1978

A mechanism for the growth of thin metal films on inert substrates in galvanostatic metal deposition is proposed. Qualitative agreement between theoretical and experimental results was obtained.

1. Introduction

The mechanism of thin metal film formation on an inert substrate in potentiostatic metal electrodeposition was discussed recently [1]. It was shown that coverage of the electrode surface depends on time and on current density of deposition on inert substrates. At the same time, deposition on the covered part of electrode takes place at a larger current density than on the inert substrate. Hence, a larger amount of metal must be deposited to obtain the same desired coverage than the quantity predicted from the first order relation between coverage and time.

A similar effect can be expected in the galvanostatic case. The current of deposition is divided into two parts; that on the inert substrate and that on the formed metal film. All effects of covering are related, as in the potentiostatic case, to the first one.

The formation of thin metal films in galvanostatic deposition has not been treated so far using the model given in [1], based on the work of Erdey-Gruz and Volmer [2]. However, Oberbek [3] and Nichols [4] deposited copper on platinum and showed that an electrodeposit of copper of the order of a few atoms thick behaved as a copper electrode. More recently, Brainina *et al.* [5] reported similar results for silver electrodeposition on a graphite electrode.

In these experiments the potential of the inert electrode was recorded as a function of the quantity of electrodeposited metal. The transformation of the electrode surface was taken to be complete when the film of metal gave the same potential as a massive metal.

No direct conclusions about the mechanism of first layer metal electrodeposition can be obtained from these experiments. This mechanism can be delineated in a similar way as in the potentiostatic case [1]. This is the purpose of this paper.

2. The statement of the problem

It is well known [2] that in metal electrodeposition on inert substrates two kinds of polarization curves are obtained. The first, given by Equation 1, relates the overpotential, η, and current density on the inert substrate, i_1, and the second one (Equation 2) overpotential and current density on the formed metal film, i_2. This can be due to two-dimensional nucleation on a polycrystalline inert substrate in the presence of a large number of screw dislocations. It is known that two-dimensional nucleation can be observed in situations where the number of dislocations is reduced, as in the deposition of silver on dislocation-free silver single crystal electrodes [6, 7], in nickel deposition on mercury [8], or in the formation of anodic films on mercury [9]. In these cases, monolayer by monolayer deposition takes place, each layer being formed by the lateral growth of two-dimensional nuclei developed upon the preceding layer, leading to the situation described by Gilmer [10].

In the case of metal deposition [6, 7], oscillations of overpotential are observed. This wavering of overpotential is connected with a

© 1978 *Chapman and Hall Ltd.*

reiterating two-dimensional nucleation process. In the initial stage the dislocation-free plane is wholly intact and does not expose any growth sites. When the current is switched on, the overpotential rises rapidly, increasing the probability of a two-dimensional nucleation. A nucleus may be formed when a critical value of overpotential is exceeded. Once a nucleus is formed, the plane begins to offer an increasing number of growth sites, crystallization becomes easier and the overpotential drops. Propagating over the surface, the steps surrounding the new layer reach the walls of the glass capillary and begin to disappear. With this, the number of growth sites diminishes and the overpotential rises again, making possible the nucleation of a second layer. The wavering of overpotential was not observed in galvanostatic metal deposition on polycrystalline inert substrates, with an unreduced number of dislocations. In this case [13], when the current is switched on, the overpotential rises rapidly up to some critical value for nucleation. During deposition, the overpotential changes from this nucleation overpotential to an overpotential corresponding to deposition on a massive electrode of the same metal. Hence, the change of overpotential is related to the change of coverage of the inert electrode surface deposition. In this case, nucleation takes place in non-ideal conditions, and spiral growth around screw dislocations of the substrate can be expected [11] on the part of the electrode covered with two-dimensional nuclei. In this way, deposition on the covered part of the electrode surface can be taken as the same as that on a massive electrode of the deposited metal. The current density on the uncovered part of the electrode surface will correspond to that of two-dimensional nucleation. After formation of the new phase starts, the constant apparent current density is divided into two parts; that on the inert substrate and that on the formed film. Because the current density on the formed metal film is large compared to that on the inert substrate [2], increasing coverage of the electrode leads to a decrease of overpotential. The current densities and the overpotential change according to Equations 1 and 2. If the relationships in Equations 1 and 2 are known, it is possible to relate coverage and overpotential with time and apparent current density by using the following procedure.

$$i_1 = f_1(\eta) \tag{1}$$

$$i_2 = f_2(\eta). \tag{2}$$

By elimination of η from Equations 1 and 2 one obtains

$$i_2 = \phi_1(i_1). \tag{3}$$

Apparent current density, i, is constant, and for coverage θ, can be written

$$i = i_1(1-\theta) + i_2\theta. \tag{4}$$

Taking into account Equation 3 one can write

$$i = i_1(1-\theta) + \phi_1(i_1)\theta \tag{5}$$

or

$$i_1 = \phi_2(i, \theta). \tag{6}$$

The change of coverage with time, t, of deposition is given by [1]

$$\frac{d\theta}{dt} = ki_1(1-\theta) \tag{7}$$

where k is a constant. The constant k relates the quantity of electrodeposited metal on the inert substrate to the corresponding coverage of electrode surface. Hence, k depends on the orientation of the nuclei. Pangarov and Velinov [12] showed that for this system (silver on platinum) there are five regions of overpotential in which the obtained nuclei are all oriented along the same crystallographic axis. In these intervals of overpotential, k is constant, but because the difference in the number of atoms per square centimeter of different crystal planes can not be very great, in the first approximation k can be taken as constant in all regions of overpotential applied.

Substitution of i_1 from Equation 6 into Equation 7 gives

$$\frac{d\theta}{dt} = k\phi_2(i, \theta)(1-\theta) \tag{8}$$

or in the integral form

$$\theta = \psi_1(i, t). \tag{9}$$

In this way, the coverage of the electrode is related to the apparent current density and time of deposition. Taking into account Equations 1 and 2, Equation 9 can be rewritten as

$$i = f_1(\eta)[1-\psi_1(i, t)] + f_2(\eta)\psi_1(i, t) \tag{10}$$

giving the possibility of relating η, after nucleation has been started, to t, by

$$\eta = \psi_2(i, t). \tag{11}$$

The change of overpotential in galvanostatic deposition before nucleation was given by Gucov [13] and Klapka [14].

3. Experimental

The deposition of silver was carried out onto a platinum electrode from 0·05 M $AgCH_3COO$ in aqueous 0·1 M $NaCH_3COO$ in an open cell. The standard galvanostatic circuitry was used throughout the work. The temperature of the cell was maintained at 22·0 ± 0·1° C.

The platinum electrode was cleaned by anodic treatment (2 h at 1·1 V versus standard hyrdogen electrode).

4. Results and discussion

Typical experimental results obtained in this work are shown in Fig. 1. The shape of the overpotential–time relationships is the same as earlier reported by Gucov [6]. From the overpotential–time relationships, similar to those presented in Fig. 1, overpotentials of nucleation and of deposition under steady-state conditions were extracted and plotted versus current density in Fig. 2. It is seen from Fig. 2 that for current densities larger than 1·5 mA cm^{-2} polarization curves can be approximated by two parallel straight lines. For current density i, the initial overpotential is that of nucleation, η_1; the steady-state overpotential, η_2, corresponds to deposition on a completely covered inert substrate. During covering of the inert substrate, the overpotential takes all values between these two overpotentials, as can be seen from Figs. 1 and 2.

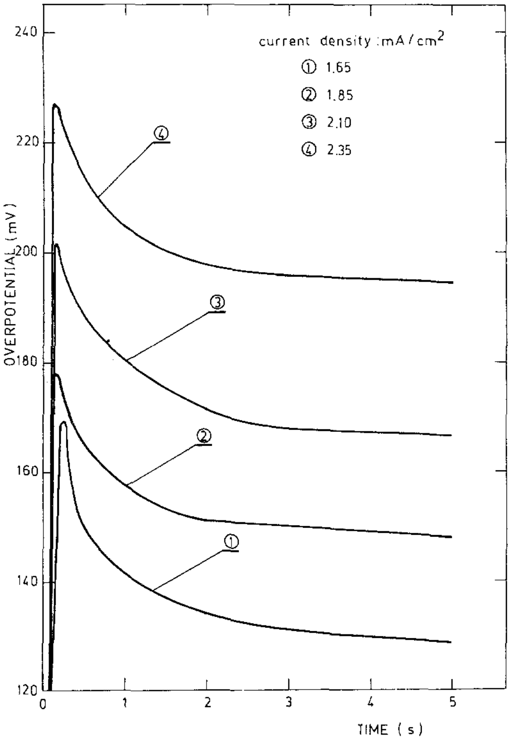

Fig. 1. Overpotential–time relationships obtained during galvanostatic deposition of silver on platinum with different current densities.

In the case when the polarization curves are two parallel straight lines it is easy to relate coverage and overpotential with time and apparent current density. Equations 1 and 2 can be, in this case, rewritten as

$$i_1 = C(\eta - \eta_0) \tag{12}$$

and

$$i_2 = C\eta \tag{13}$$

where C is a constant and η_0 the critical overpotential of nucleation. The elimination of η from Equations 12 and 13 gives

$$i_2 = i_1 + C\eta_0. \tag{14}$$

Substitution of i_2 from Equation 14 in Equation 4 gives

$$i = i_1 + C\eta_0\theta. \tag{15}$$

By substitution of i_1 from Equation 7 in Equation 15 one obtains

$$i = \frac{d\theta}{dt}\frac{1}{k(1-\theta)} + C\eta_0\theta \tag{16}$$

or

$$\frac{1}{k}\frac{d\theta}{dt} = i - \theta(i + C\eta_0) + C\eta_0\theta^2. \tag{17}$$

The solution of Equation 17 is given by

$$\theta = \frac{i\{1 - \exp[kt(i - C\eta_0)]\}}{C\eta_0 - i\exp[kt(i - C\eta_0)]}. \tag{18}$$

It is seen that the proposed mechanism is valid for $i > C\eta_0$. It is easy to show that $\theta = 0$ for $t = 0$ and $\theta \to 1$ for $t \to \infty$. By combining Equations 12 and 15 one obtains

$$i = C\eta - C\eta_0(1 - \theta). \tag{19}$$

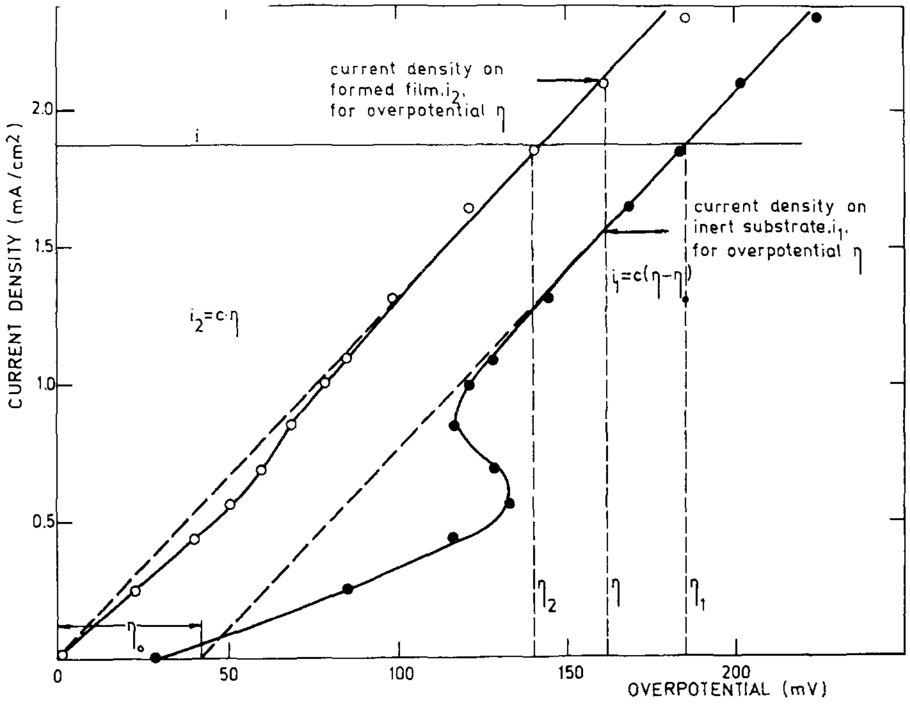

Fig. 2. Current density (i_1, i_2)–overpotential relationships.

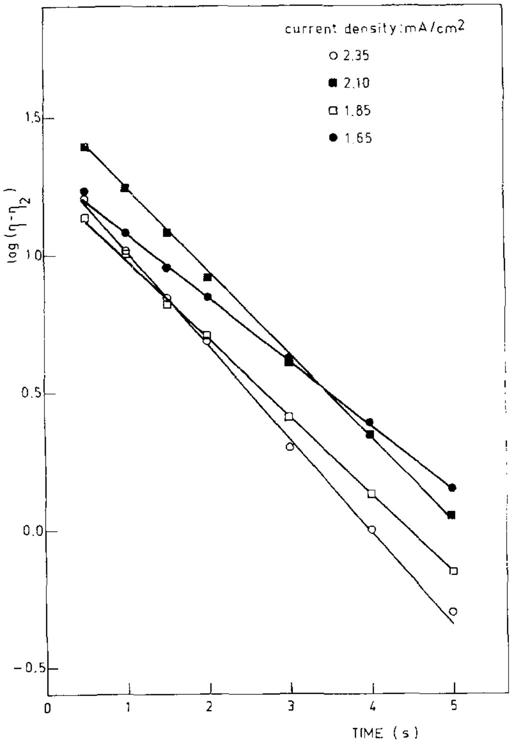

Fig. 3. log ($\eta - \eta_2$)–t relationships obtained using Equation 22 and the data from the diagrams presented in Fig. 1.

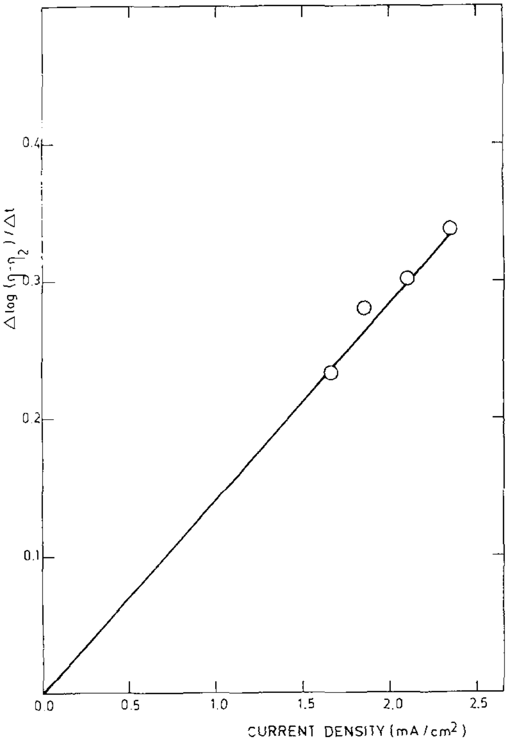

Fig. 4. The slopes extracted from the straight lines presented in Fig. 3 as a function of current density.

Hence, the mathematical model given obeys all requirements of the physical model of the system.

To confirm this mechanism, the relationship between overpotential and time must be established, because θ cannot be measured directly. In order to obtain this relationship Equation 19 must be rewritten in the form

$$\eta = i/C + \eta_0(1-\theta). \tag{20}$$

It is obvious that for $\theta = 0, \eta = \eta_1$ and for $\theta = 1$, $\eta = \eta_2$. On the basis of Equations 13 and 18, Equation 20 can be written now as

$$\eta = \eta_2 + \eta_0 \frac{C\eta_0 - i}{C\eta_0 - i \exp\,[kt(i - C\eta_0)]} \tag{21}$$

or

$$\eta = \eta_2 + \eta_0 \exp\,(-kit) \tag{22}$$

for $i \gg C\eta_0$.

For current densities corresponding to the overpotential–time relationships presented in Fig. 1 $i \gg C\eta_0$ and polarization curves are two parallel straight lines. Hence, it can be expected that Equation 22 can be applied to the plots presented in Fig. 1. In Fig. 3 the log $(\eta - \eta_2)$–t plots corresponding to the η–t relationships from Fig. 1 are presented. The straight lines obtained confirm well the proposed mechanism. Further proof is given by the graph presented in Fig. 4. The slopes extracted from the straight lines given in Fig. 3 are plotted versus apparent current density. It is seen that a straight line is obtained. This means that k is really constant in this region of current density and overpotential values, as was assumed earlier.

On the basis of the above discussion it can be concluded that the mathematical model given is qualitatively in good agreement with the experimental results obtained.

References

[1] K. I. Popov, D. N. Keča, and G. R. Ostojić, *J. Appl. Electrochem.* **6** (1976) 425.

[2] T. Erdey-Gruz and M. Volmer, *Z. Phys. Chem.* **A157** (1931) 182.

[3] A. Oberbek, *Ann. Physik 3* **31** (1887) 337.

[4] M. L. Nickols, *J. Amer. Chem. Soc.* **57** (1935) 267.

[5] J. Z. Brainina, N. K. Khiwa and V. B. Belyavskaiya, *Elektrokhimiya* **1** (1965) 311.

[6] E. Budewski, W. Bostanoff, T. Witanoff, Z. Stoinof Z. Stoinoff, A. Kotzeva and R. Kaishew, *Electrochim. Acta* **11** (1966) 1697.

[7] R. Kaishew and E. Budewski, *Contemp. Phys.* **8** (1967) 489.

[8] M. Fleischmann, J. A. Harrison and H. R. Thirsk, *Trans. Faraday Soc.* **61** (1965) 2742.

[9] A. Bewick, M. Fleischmann, H. R. Thirsk, *ibid* **58** (1962) 2200.

[10] G. H. Gilmer, The Chemical Society, Faraday Division, Symposium no. 12, 'Electrocrystallization, Nucleation and Phase Formation', paper No. 5.

[11] V. Bostanov, R. Rusinova and E. Budevski, *Comm. Dept. Chem. BAN* **2** (1969) 885.

[12] N. A. Pangarov and V. Velinov, *Electrochim. Acta* **11** (1966) 1753.

[13] I. Gucov, *Izv. Inst. Fizikochim. BAN* **4** (1964) 69.

[14] V. Klapka, *Coll. Czech. Chem. Communs.* **36** (1971) 1181.