

Elimination of nucleation exclusion zones by electrodeposition at a reversing current

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Elimination of nucleation exclusion zones by electrodeposition at a reversing current (RC) in the seconds time range is considered. It is shown that nucleation exclusion zones formed in constant regimes can be eliminated by a reversing current only if the deposition process is under full diffusion control.

Key words: metal deposition, reversing current, exclusion zones.

The formation of a surface metal film on an inert substrate during electrochemical metal deposition was discussed recently¹ on the basis of the Markov *et al.*² and the Klapka³ theories. According to Markov *et al.*² nucleation exclusion zones are formed due to electric field deformation in the vicinity of the growing grains; according to Popov *et al.*,¹ the nucleation exclusion zone radius depends on the exchange current density of the deposition process, because the critical overpotential for nucleation to occur depends on the deposition process exchange current density.^{1,3} An excellent qualitative agreement between theory and practice was obtained.¹ It was shown that the mechanism of surface film formation strongly depends on the exchange current density value of the deposition process. At high exchange current densities, zero nucleation zones exist which determine the saturation nucleus density; in the opposite case, the saturation nucleus density depends on the number of active sites.⁴ It is obvious that in the latter case a much lower quantity of electrodeposited metal is required for compact surface film formation. It is known that the nucleation exclusion zones existing during the deposition of some metals (metals with a high value of the exchange current density) from simple salt solutions can be eliminated by deposition from complex salt solutions due to a decrease in the exchange current density,⁵ as well as by the addition of some surface active substances.⁶ The elimination of nucleation exclusion zones during deposition from pure simple salt solutions has not been realized so far. The purpose of this work was to confirm the Markov *et al.*² theory and to try to eliminate nucleation exclusion zones by electrodeposition at a reversing current (RC).

EXPERIMENTAL

a) Silver was chemically deposited onto a platinum electrode with deposited silver grains (substrate I), which was obtained, in the work of Popov *et al.*¹ in the following way:

Silver was electrochemically deposited on a platinum plane cathode with an area of 2.5 cm². The deposition was carried out potentiostatically from 0.1 M AgNO₃ in 0.5 M HNO₃, at room temperature in an open cell. The deposition overpotential was 6 mV and deposition time was 45 min. The anode and reference electrodes were of pure silver.

The chemical deposition of silver was carried out using the following solutions:

Solution A: AgNO₃ – 5 g/L; NH₃(25%) – 10 ml/L; KOH – 5 g/L.

Solution B: 1.3 g C₆H₁₂O₆ was dissolved in 25 cm³ of doubly distilled water and one drop of conc. HNO₃ was added. The obtained solution was boiled for 2 min and after cooling diluted with 25 cm³ 96% C₂H₅OH. 10 cm³ of solution A was poured into a 100 cm³ beaker then substrate I was placed in it and 0.5 cm³ of solution B added. The obtained solution was heated for 5 min at a temperature of 50 °C.

b) Silver was electrodeposited by RC onto a platinum electrode with silver grains around which the nucleation exclusion zones were formed (substrate II). Substrate II was obtained in the work of Popov *et al.*¹ in the following way:

Silver was electrochemically deposited on substrate I galvanostatically from 0.1 M AgNO₃ in 0.5 M HNO₃, at room temperature in an open cell. The deposition current density was 2.9 mA/cm² and the deposition time was 2 min. The anode and reference electrodes were of pure silver.

The parameters which determine the shape of the RC were were:

1. $j_{av} = 0.425 j_L$, $j_A = 0.9 j_L$, $T_p = 9.5 s$, $r_1 = 5/14$

2. $j_{av} = 0.850 j_L$, $j_A = 1.8 j_L$, $T_p = 9.5 s$, $r_1 = 5/14$

The morphology of the metal deposits was investigated by means of scanning electron microscopy, using a JEOL T-20 microscope.

RESULTS AND DISCUSSION

The assumption that the formation of nucleation exclusion zones is due to the deformation of the electric field around growing grains can be verified by the electroless deposition of silver on substrate I. It can be seen from Fig. 1 that there are no nucleation exclusion zones around grains, confirming the above assumption. It can also be seen that electroless deposition takes place over the whole of substrate I, *i.e.*, on the platinum electrode and on the silver grains (Fig. 1).

Silver electrodeposited on substrate II by reversing current is shown in Fig. 2. In the first case (Fig. 2a), the average current density was 0.425 j_L and the amplitude current density was 0.9 j_L . Deposition of silver takes place only on the silver grains and nucleation exclusion zones can be clearly seen (Fig. 2a). Also in RC deposition, but under different condition, the opposite situation appears (Fig. 2b). In this case, the average current density and the amplitude current density were double those in the first case. Deposition takes place on the silver grains and on the platinum electrode and nucleation exclusion zones do not exist (Fig. 2c). This difference is due to the different shapes of the RC wave used in the deposition.

According to Markov *et al.*,² the nucleation exclusion zone radius, r , in an ohmic-controlled deposition is given by:

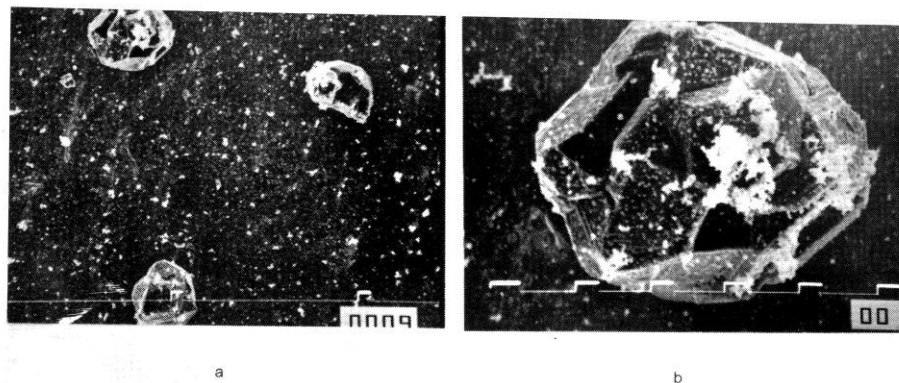


Fig. 1. Silver chemically deposited on substrate I (platinum electrode with electrodeposited silver grains). Magnification: a) $\times 500$; b) $\times 2000$.

$$r = f \frac{E}{E - \eta_c} \rho \quad (1)$$

where η_c is the critical overpotential for nucleation to occur, E is the cell voltage, f a numerical factor and ρ the radius of the nucleus.

In the first case (Fig. 2a), the system was not under full diffusion control of the deposition process and the value of the overpotential at the end of the cathodic pulse

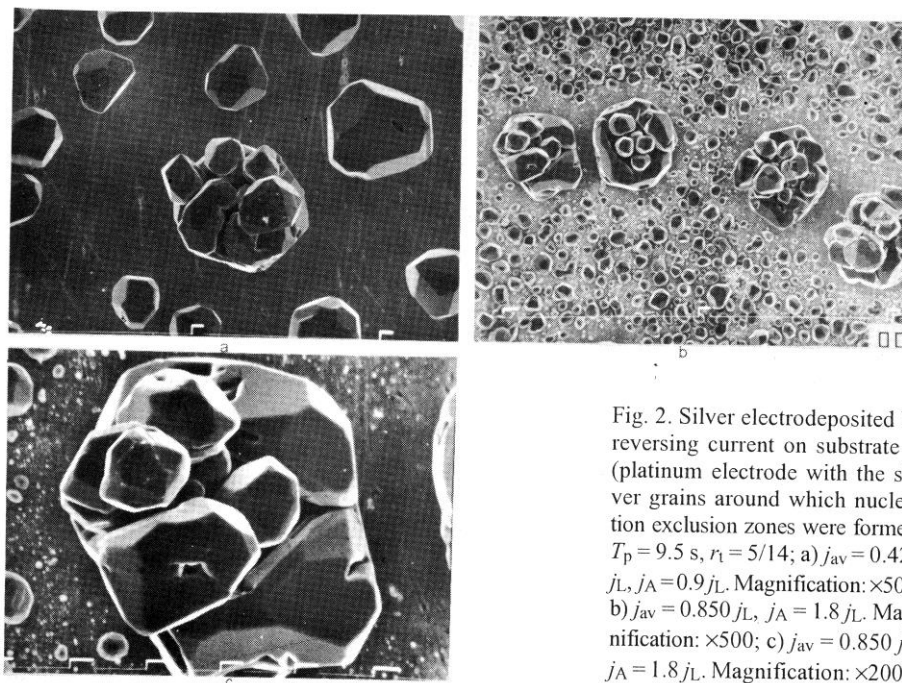


Fig. 2. Silver electrodeposited by reversing current on substrate II (platinum electrode with the silver grains around which nucleation exclusion zones were formed). $T_p = 9.5$ s, $r_t = 5/14$; a) $j_{av} = 0.425$ j_L , $j_A = 0.9$ j_L . Magnification: $\times 500$; b) $j_{av} = 0.850$ j_L , $j_A = 1.8$ j_L . Magnification: $\times 500$; c) $j_{av} = 0.850$ j_L , $j_A = 1.8$ j_L . Magnification: $\times 2000$.

was not larger than 110 mV. In the second case (Fig. 2b), the overpotential at the end of the cathodic pulse was 500–900 mV, meaning that the deposition time was larger or close to the transition time in the system under consideration. The absence of nucleation exclusion zones in the second case can be explained by Eq. (1) under the assumption that E in Eq. (1) represents the overall deposition overpotential.

In a diffusion controlled reaction, with the charge transfer in virtual equilibrium, *i.e.* the charge transfer reaction is assumed to have a high exchange current density ($j_0 \rightarrow \infty$), the activation overpotential tends to zero. On consumption of the depositing metal ions by the charge transfer reaction, the concentration of the ions at the surface of the electrode decreases from its initial value, *i.e.*, from the bulk concentration, c_0 . Since the diffusion process cannot replenish all of the consumed ions, the concentration gradually decreases and after a period of time, termed the transition time, becomes close to zero.

The overpotential amplitude, η_A , in reversing current in the seconds time range is given by:

$$\eta_A = \frac{b_c}{2.3} \ln \frac{j_A}{j_0} + \frac{b_c}{2.3} \ln \frac{c_0}{c(0,t)} \quad (2)$$

The surface concentration of depositing ions, $c(0,t)$, the bulk concentration of depositing ions, c_0 , and the transition time, τ , can be related by:

$$\frac{c(0,t)}{c_0} = \frac{\tau^{1/2} - t^{1/2}}{\tau^{1/2}} \quad (3)$$

According to Eqs. (2) and (3), the amplitude overpotential can be written as follows:

$$\eta_A = \frac{b_c}{2.3} \ln \frac{j_A}{j_0} + \frac{b_c}{2.3} \ln \frac{\tau^{1/2}}{\tau^{1/2} - t^{1/2}} \quad (4)$$

When $t \rightarrow \tau$, the amplitude overpotential $\eta_A \rightarrow |-\infty|$. Consequently, after the transition time, the amplitude overpotential represents the diffusion overpotential of the deposition process.

Therefore, when there is full diffusion control of the deposition process, the cell voltage, $E \rightarrow |-\infty|$. According to Eq. (1), if $E \rightarrow |-\infty|$, the nucleation exclusion zone radius, $r \rightarrow 0$, *i.e.*, nucleation exclusion zones are eliminated. In the first case, the deposition is not under full diffusion control, hence, the amplitude overpotential is very small and the cell voltage $E \not\rightarrow |-\infty|$. According to Eq. (1), when $E \not\rightarrow |-\infty|$, the nucleation exclusion zone radius, $r \rightarrow 0$ and so nucleation exclusion zones exist.

Hence, it is possible to eliminate nucleation exclusion zones by electrodeposition at a reversing current in seconds time range only if the system is under full diffusion control of deposition process. Then, the cell voltage, E , in Eq. (1)

represents the overall deposition overpotential, rather than the ohmic drop voltage in the cell, as was shown by Markov *et al.*² This means, from the practical point of view, that such a regime can be applied during the first RC pulses. After the first pulses, the current density has to be decreased in order to avoid dendritic growth initiation.

NOTATION

| | |
|----------|--|
| b_c | slope of cathodic Tafel line |
| c_0 | bulk concentration of depositing ions |
| $c(0,t)$ | surface concentration of depositing ions |
| E | cell voltage |
| f | numerical factor |
| j_A | amplitude current density |
| j_{av} | average current density |
| j_L | limiting current density |
| j_0 | exchange current density |
| r | radius of the nucleation exclusion zone |
| r_t | anodic to cathodic time ratio |
| t | time |
| T_p | period |

Greek letters

| | |
|----------|-------------------------|
| ρ | radius of nucleus |
| η_A | amplitude overpotential |
| η_c | critical overpotential |
| τ | transition time |

ИЗВОД

ЕЛИМИНАЦИЈА ЗОНА ИСКЉУЧЕЊА НУКЛЕАЦИЈЕ ТАЛОЖЕЊЕМ РЕВЕРСНОМ СТРУЈОМ

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Разматрано је елиминисање зона искључења нуклеације електрохемијским таложењем реверсном струјом у секундном подручју. Показано је да се зоне искључења нуклеације формиране у константном режиму могу елиминисати реверсном струјом само ако је таложење под пуном дифузионом контролом.

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