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Nucleation and growth kinetics of Ag_7NO_{11} on a platinum single crystal electrode

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The process of electrochemical deposition of Ag_7NO_{11} on a platinum single crystal anode from 5 M $AgNO_3$ is investigated. The nucleation and growth rates are measured at different constant overpotentials. The orientation of the Ag_7NO_{11} crystals with respect to the substrate surface is determined in the case of deposition on glassy carbon and on the $\langle 100 \rangle$, $\langle 111 \rangle$ and $\langle 110 \rangle$ faces of a platinum single crystal.

1. Introduction

It is well known [1–3] that with anodic polarization of a platinum electrode the argentic oxysalt $Ag(Ag_3O_4)_2 NO_3$ is deposited from $AgNO_3$ aqueous solution, the overall electrochemical reaction of the process being:

$$17Ag^+ + NO_3^- + 8H_2O \longrightarrow Ag_7NO_{11} + 10Ag + 16H^+ \qquad (1)$$

It is the aim of this study to examine the nucleation and growth kinetics of this silver compound at constant overpotential.

2. Experimental details

The electrolyte was 5 M $AgNO_3$ with pH = 1.45 obtained by adding HNO_3. The temperature was kept at 35° C. The working electrode was a polyfaced platinum single crystal with a surface area of 1.4×10^{-3} cm^2 made by melting platinum wire and sealing in a glass tube. Bulk polycrystalline silver was used both as reference and counter electrode.

By polarizing the platinum electrode to a potential E in the range 1.74–1.77 V vs SHE, dark gray, bright cubooctahedral crystals were formed on the platinum surface (Fig. 1). The X-ray diffraction study (Fig. 2) showed that the deposit consisted of $Ag(Ag_3O_4)_2NO_3$ which, exposed to air, decomposed slightly to 2AgO. The equilibrium potential of the macrocrystals of $Ag(Ag_3O_4)_2NO_3$ in the working electrolyte was found to be $E_0 = 1.59$ V vs SHE. The nucleation and the growth overpotentials η were defined as the difference between the actual potential E of the platinum electrode and the equilibrium potential E_0 of Ag_7NO_{11} ($\eta = E - E_0$).

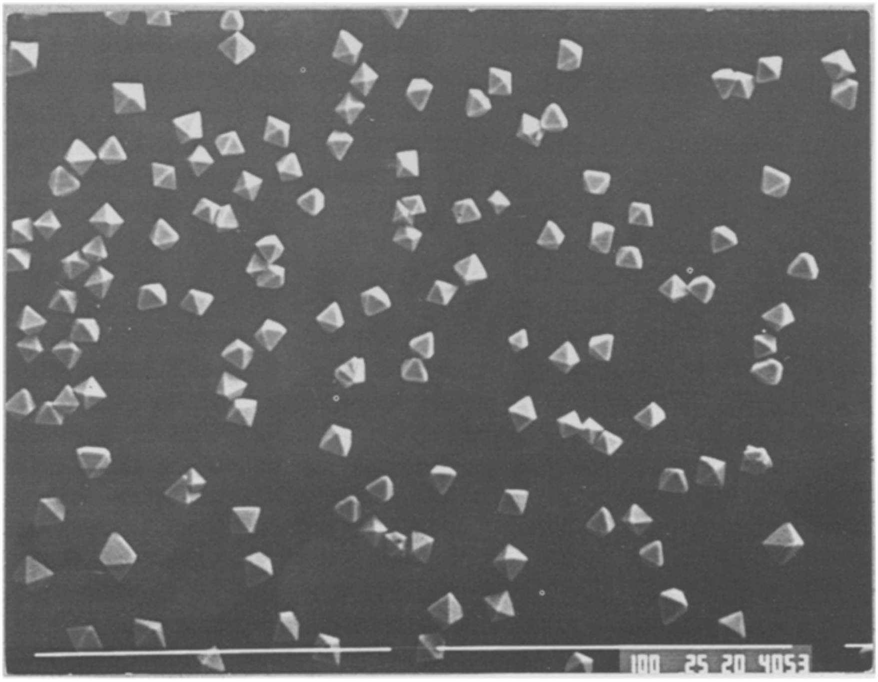

Fig. 1. Ag_7NO_{11} crystals formed on a platinum single crystal electrode. Magnification 500×.

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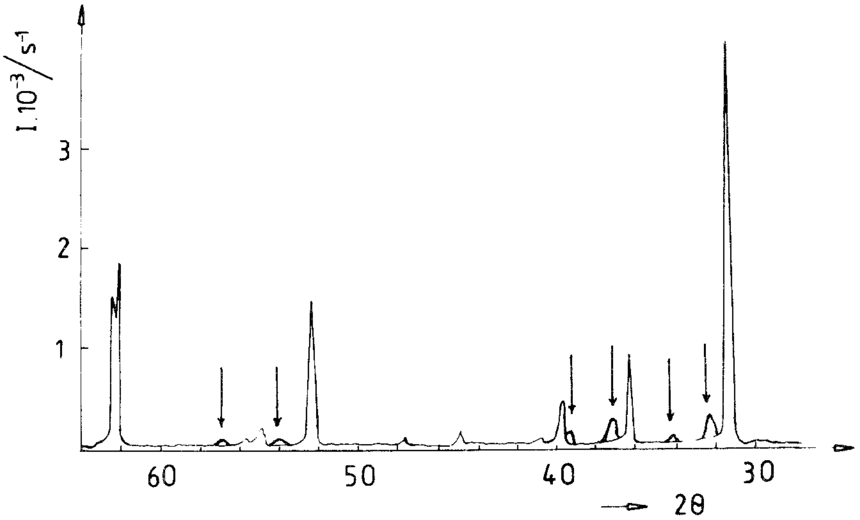

Fig. 2. X-ray diffraction pattern of Ag_7NO_{11} giving the intensity I as a function of the diffraction angle 2θ. The peaks marked by arrows correspond to 2AgO and appear after exposing the sample to air for 1 month.

3. Results and discussion

3.1. *Nucleation kinetics of Ag_7NO_{11}*

The rate, I, of nucleus formation of Ag_7NO_{11} was measured directly from the slope, dN/dt, of the number of nuclei (N)-time (t) relationships (Fig. 3) obtained at different constant overpotentials η*.

The nucleation $N(t)$ relationships given in Fig. 3 show that, after an induction period, the nucleation proceeds with a constant, stationary rate $dN/dt = I_{st}$. According to the atomistic theory of electrochemical nucleation (see Ref. [4] and the references cited therein) the overpotential dependence of this quantity is given by:

$$I_{st} = z_0 w_{+k} \exp\left[-\frac{\phi(n_k)}{kT}\right] \exp\left[\frac{n_k ze\eta}{kT}\right] \qquad (2)$$

where z is the valency of the depositing ions, e is the elementary electric charge, n_k is the number of building elements in the critical nucleus and w_{+k} is a frequency factor depending on the mechanism of critical nucleus formation. The quantity $\phi(n_k)$ accounts for the energy contribution of both the 'nucleus–substrate' and the 'nucleus–solution' interfaces and z_0 is the number of sites on the substrate where nucleation proceeds with a measurable rate.

Figure 4 presents the experimental data for I_{st} plotted in semilogarithmic coordinates ln I_{st} vs η. From the slope of the straight line with $z = 1$ one obtains $n_k = 1$ molecule Ag_7NO_{11}. It should be noted, however, that this estimate does not take into account the possible overpotential dependence of w_{+k} which is not known in this complicated case of phase formation.

As for the induction periods of the nucleation process (the intercepts from the time axis in Fig. 3) it was found that, similarly to other cases of electrochemical phase formation [5], they decrease when increasing the overpotential following an exponential law of the type $t_0 \sim \exp(-a\eta)$, a being equal to 100 in the case under consideration.

3.2. *Growth kinetics of Ag_7NO_{11}*

The growth kinetics of Ag_7NO_{11} were examined by measuring the growth current of single Ag_7NO_{11} crystals at constant overpotential. Series of current transients obtained at growth overpotentials in the

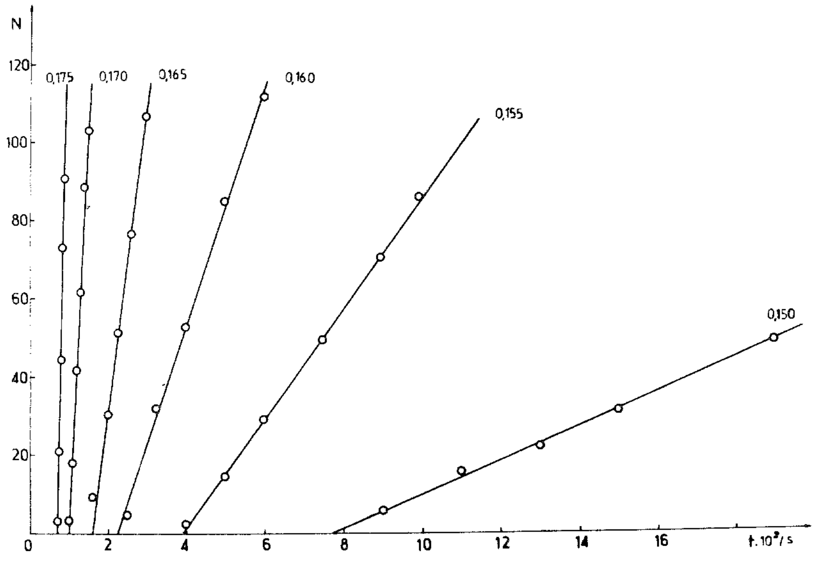

Fig. 3. Number of nuclei–time relationships obtained at different overpotentials marked by figures in V.

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* The double potential step technique used to form and visualize the Ag_7NO_{11} nuclei on the platinum surface is described in detail in [4].

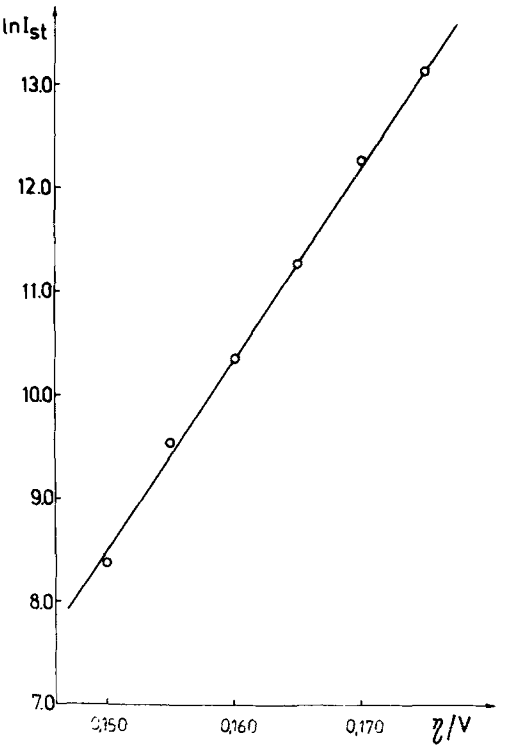

Fig. 4. Overpotential dependence of the stationary nucleation rate I_{st}.

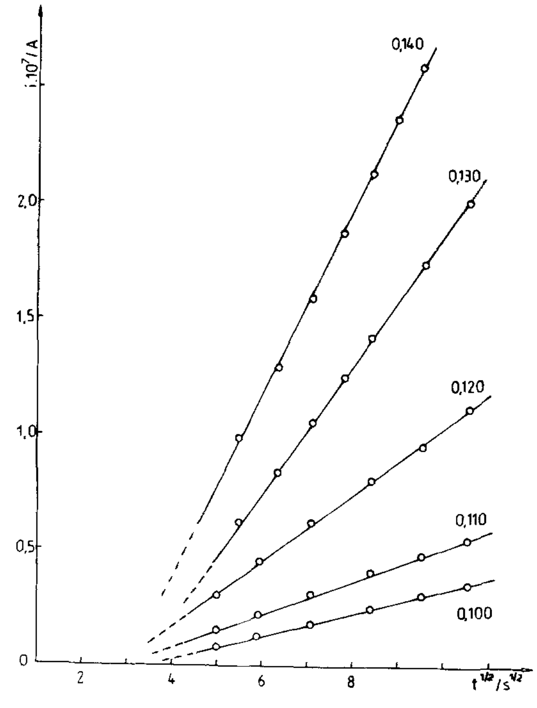

Fig. 6. i vs $t^{1/2}$ plots of the current transients from Fig. 5.

range 0.100–0.140 V are shown in Fig. 5. In Fig. 6 the data for i are plotted in coordinates i vs $t^{1/2}$ and give straight lines at long times, as expected, when transport limitations determine the growth of a single hemispherical crystal [6]. The existence of transport limitations was additionally confirmed by the nucleation exclusion zones arising around the growing Ag_7NO_{11} macroclusters. Such zones were visualized (Fig. 7) by using the triple-step potential technique as suggested in [7].

Finally Fig. 8 demonstrates the overpotential dependence of the rate constants $A = di/dt^{1/2}$ which proves to be much stronger than that theoretically predicted for the case of simple transport limitations. The explanation of this result should probably be sought in some complicated growth mechanism corresponding to the overall electrochemical reaction (Equation 1).

3.3. *Orientation of the Ag_7NO_{11} crystals with respect to the substrate surface*

An important question related to the phase formation process is: how are the clusters of the new phase oriented with respect to the substrate surface?

In the case under consideration the answer to this question was given by inspecting electron micrographs of 651 Ag_7NO_{11} crystals deposited on the cubic ⟨100⟩, octahedral ⟨111⟩ and rombododecahedral ⟨110⟩ crystallographic faces of the platinum single crystal anode.

The results of the statistics are schematicaly given in Fig. 9a where P⟨hkl⟩ denotes the percentage of Ag_7NO_{11} crystals contacting the corresponding plati-

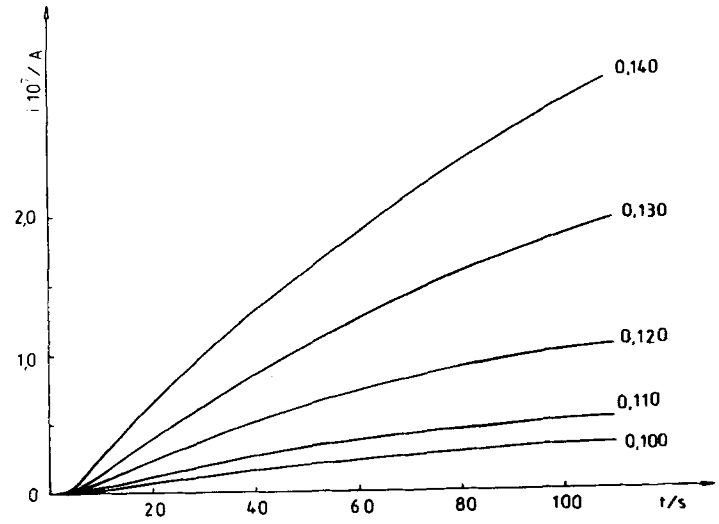

Fig. 5. Current of growth of single Ag_7NO_{11} crystals obtained at different overpotential marked by figures in V.

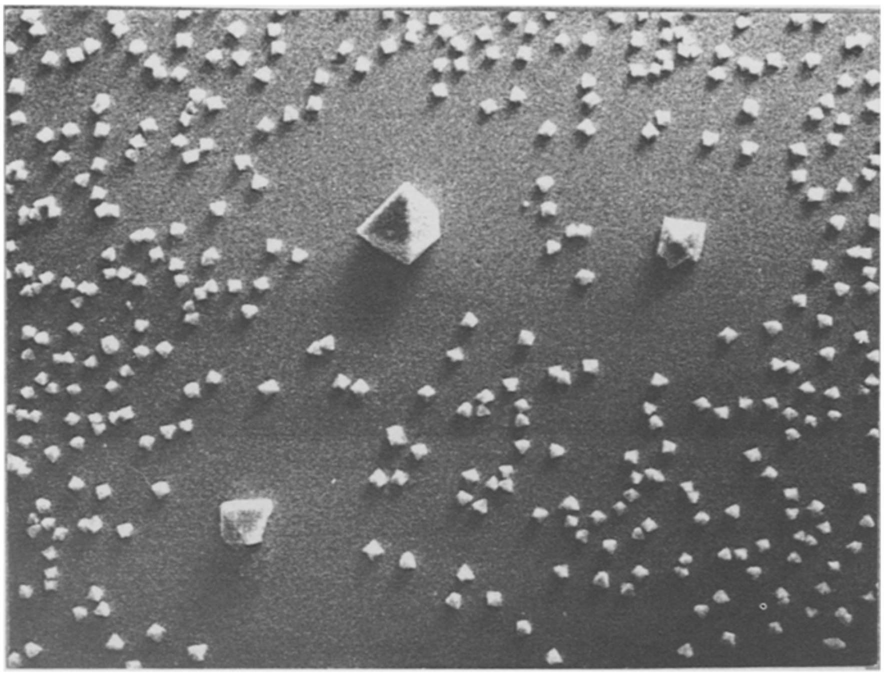

Fig. 7. Nucleation exclusion zones arising around growing Ag_7NO_{11} macrocrystals. Magnification 1000 ×.

num face with their ⟨100⟩, ⟨111⟩ and ⟨110⟩ faces, respectively. For comparison Fig. 9b shows the results for P⟨hkl⟩ obtained when Ag_7NO_{11} crystals were deposited on an amorphous glassy carbon substrate.

As is seen from Fig. 9 the platinum single crystal surface has no strong epitaxial influence on the Ag_7NO_{11} crystals. This might be due either to the significant difference in the lattice parameters of Pt (d = 3.95 Å) and Ag_7NO_{11} (d = 9.87 Å) or to the fact that under the conditions of this experiment (pH = 1.45, E = 1.79 V vs SHE) the platinum substrate is covered by an oxygen-containing surface layer [8]. Obviously the latter can mask the influence of the original single crystal surface.

It is to be pointed out also that the final crystal orientation depends not only on the 'substrate–deposit' interaction but also on the nucleation and growth conditions in the corresponding experimental system. Therefore it would be interesting to study the Ag_7NO_{11} orientation on platinum and glassy carbon at different overpotentials and electrolyte temperatures. Of course, when carrying out such experiments one should always bear in mind that misleading results could be obtained if using a roughly polished electrode surface. For instance, a true ⟨100⟩ orientation (Fig. 10a) may look like a ⟨111⟩ orientation with respect to the flat surface if the crystallite is formed in a groove or on a macrostep of the substrate. Although it is statistically likely that such errors would be par-

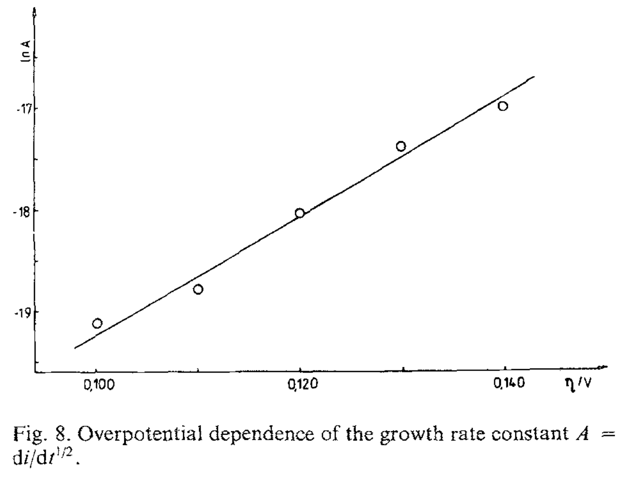

Fig. 8. Overpotential dependence of the growth rate constant $A = \mathrm{d}i/\mathrm{d}t^{1/2}$.

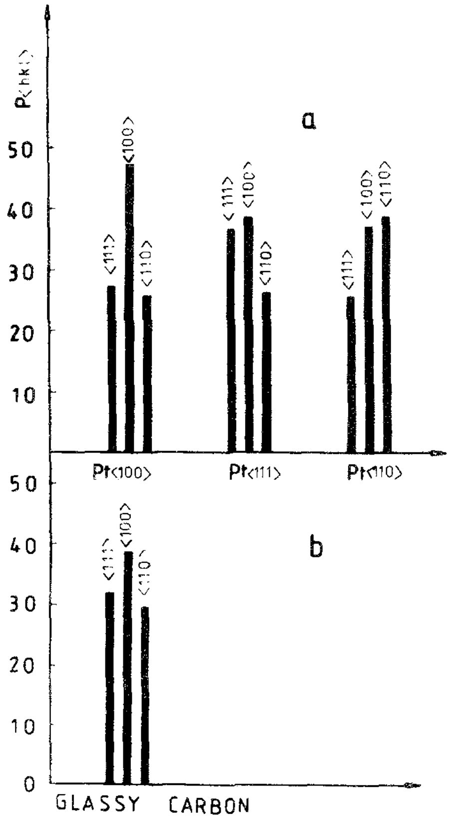

Fig. 9. Schematic diagram representing the orientation of Ag_7NO_{11} crystals on (a) platinum, η = 0.180 V and (b) glassy carbon, η = 0.200 V.

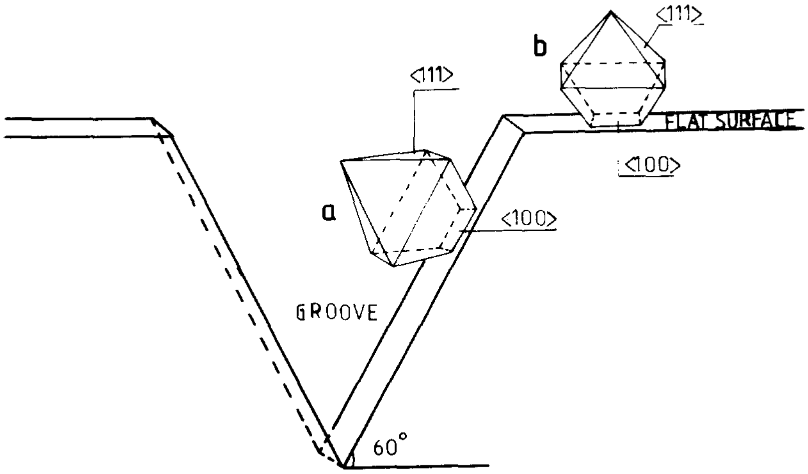

Fig. 10. Schematic representation of a crystal with ⟨100⟩ orientation formed in a groove (a) and on the flat surface (b).

tially compensated in a large sample the melted mirror-bright platinum surface seems to be more suitable for such orientation studies than the mechanically polished glassy carbon substrate.

Acknowledgement

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