ALUMINUM-ELECTROCRYSTALLIZATION FROM METAL–ORGANIC ELECTROLYTES

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Abstract—Aluminum electrodeposition from aprotic solutions of the organic complex $KF. 2Al(C_2H_5)_3$ on polycrystalline aluminum and vitreous carbon is described for potentiostatic and voltage pulse conditions.

Near the equilibrium of the aluminum electrode, below currents of about -3 mA cm^{-2} , electron transfer controls the deposition rate. Stationary polarizations over -0.1 V generate a material transport limitation which was controlled and eliminated by the rotating disk electrode technique. Extending the overvoltage to -0.1 to -0.3 V a slow chemical process characterized by a reaction current of $ca - 5 \text{ mA cm}^{-2}$ precedes charge transfer. Above -0.3 and -0.7 V two further deposition mechanisms possibly involving slow chemical and crystallization steps were observed.

On a foreign substrate, *ie* vitreous carbon, it was found that peripheral kinetically controlled growth of instantaneously formed two-dimensional plates takes place on top of plates so as to produce three-dimensional nuclei which then grow by a transport limited mechanism.

1. INTRODUCTION

Interest in the preparation of aluminum deposits has steadily increased during the last decades as the excellent corrosion resistance of aluminum[1] permits the solution of many engineering problems. Another advantage of high-purity aluminum coatings is the fact that they are readily anodized, and the oxide layer thus attained exhibits very good mechanical properties and decorative appearance.

Several procedures can be employed for the deposition of aluminum on various metals—mainly on steels—such as metal spraying, hot-dipping, vacuum deposition, cladding *etc*. These techniques are rather expensive and often impracticable because of possible damage of the specimen at high temperatures employed.

The problem of electrodeposition of aluminum at moderate temperatures attracted the attention of many research workers since the end of the century[2-4]. Interesting advances in this field have been made in ether-based baths 5-77. Organo-aluminum baths of the type MeX. 2AlR₃ have been suggested for the electrolysis of aluminum[8, 9], where Me was preferentially Na and X equal F, respectively. Several studies on the conductivity[10, 11] and the electrolysis products [12] led to various views on the dissociation equilibria involved in the electrolysis[8, 10, 12-15] on a hypothetical basis. The high purity of the metal deposit could be confirmed[16, 17]. Since then a systematic development to a technical deposition process has been conducted[17-19] successfully. A decisive progress was made by tailoring

organometallic electrolytes for the electrodeposition of aluminum according to the so-called SIGAL®process[19] that can consist in a toluene solution of a metal fluoride compound of the general formula MeF. $[(m-n)Al(C_2H_5).nAlR_3]$ wherein Me is potassium, rubidium or caesium, R is H or C_xH_{2x+1} , x being an integer selected from 1 and 3-8, m is a number from 1.3 to 2.4, and n is a number from 0.1 to 1.1 (m being larger than 2n). The SIGAL®-process leads to optimum deposition rate, throwing power, electrolyte conductivity, and solubility.

The object of this work is the investigation of potentiostatic polarizations with the aim of a systematic understanding of the electrochemical processes involved. The results are interpreted in terms of current-potential characteristics, exchange current densities, and apparent Tafel coefficients. In the past, models of the mechanism of electrochemical metal deposition have been based on measurements made by deposition on to solid substrates, mostly of the same metal. However, such metal surfaces assume a complex structure during growth. It is therefore clearly essential to investigate metal deposition before the complex structure of the metal surface has been formed. We investigated the aluminum deposition when metal-complex ions are deposited as metal not only on polycrystalline aluminum but also on an inert substrate, ie vitreous carbon, paying attention to the early stages of the reaction. This has the advantage that the initial steps of growth can be studied when the nuclei may be still reasonably dislocation-free, and the currents are truly controlled by the kinetics of the electrocrystallization reaction.

2. EXPERIMENTAL

The electrolyte was prepared by heating an analytical grade toluene solution of $Al(C_2H_5)_3$ (Schering) with a stoichiometric amount of analytical grade potassium fluoride at about 100°C under argon to give a dilution of four moles of toluene to one mole of KF.

The electrochemical cell could be kept under solvent saturated dry argon gas, and was thermostated by a silicon oil circuit at $103 \pm 3^{\circ}$ C. As reference served an aluminum rod connected to the working electrolyte by a Luggin-capillary. The counter-aluminum-electrode was separated from the working compartment by a fine glass diaphragm. The electrode disks had an area of 0.20 cm², and were fitted into cylinders of Macor[®] glass ceramics. This material was the only machinable insulating substance that proved chemically and thermally stable in this organic system. The electrode surfaces were polished by diamond pastes with a final corn size of $ca 0.5 \mu m$. An ultrasonic bath served to remove loose particulates from this process. The aluminum surface was etched in a special solution ("Trinorm Al") optimized to remove aluminum oxide. A fresh aluminum layer was deposited on this surface prior to measurements. A conventional potentiostatic three-electrode configuration with *iR*-compensation was employed. Best results for the evaluation of the electrolyte resistance between the working electrode and the tip of the Luggin capillary were achieved by increasing the frequency of a 20 mV sinus signal till the current amplitude remained independent of frequency. The quotient of the 20 mV over the amplitude gave the required resistance. Fast current transients were recorded by a digital storage oscilloscope (Tektronix 336) to produce hard copies on a x-y recorder.

3. RESULTS AND DISCUSSION

3.1 Stationary deposition on aluminum substrates

Current-overvoltage $(j-\eta)$ characteristics proved independent of the sweep rate up to 1000 mV s⁻¹ in the range of $-1.1 < \eta < +0.5$ V. The aluminum deposition currents on polycrystalline aluminum substrates were recorded at 50 mV s⁻¹, and therefore can be regarded stationary. The disk electrode rotation rates (m) were varied to control the diffusion layer of possible aluminum depolarizer complexes. Up to m=500 min⁻¹ currents increased till they practically stayed at the level attained at this rotation rate. All rates but 0 and 500 min⁻¹ have been omitted in Fig. 1 for clarity.

The cathodic deposition range showed three current waves called A, B and C in Fig. 1. Between $\eta = 0$ and $\eta = -0.3$ V the current rapidly reaches a plateau which slightly is controlled by the rotation rate m. Between $\eta = -0.3$ and -0.7 V a second, flat wave between ca - 6 and -20 mA cm⁻² occurs. Above $\eta = -0.7$ V the third distinct wave C is generated which is characterized by a stronger convection dependence than A and B. Diffusion rate control has to be climinated to uncover subsequent slow kinetic processes which might be of the same order of magnitude. This was achieved at the rotating disk electrode by employment of the extended so-called "mixed-

control"-Levich-equation[20, 21]:

$$1/j = 1/j_r + 1/A \cdot m^{-0.3}, \tag{1}$$

where A contains diffusional parameters[21]. The second term on the right hand side describes the diffusional component, and is separated from the first term representing a kinetic limiting current. A linear plot of $1/j vs 1/m^{0.5}$ in Fig. 2 can be extrapolated to $m^{-0.5} = 0$ yielding $1/j_r$ the reciprocal kinetic current stripped of diffusional components. These j_r results have been used to establish $\log j vs \eta$ (Tafel) plots in Fig. 3 for anodic potentials and range A, and Fig. 4 for all cathodic waves. At moderate overvoltages Fig. 3 shows Tafel-regions for both the reduction and dissolution. Anodic and cathodic Tafel-coefficients, b_+ and b_- , are equal to 0.050 ± 0.003 V. With:

$$b_{+} = 2.3 \operatorname{R} T / (z \alpha F), \qquad (2a)$$

$$b_{-} = 2.3 \text{ R} T / (z(1 - \alpha) \text{F}),$$
 (2b)



Fig. 1. Stationary $j-\eta$ relationship for the deposition of aluminum from (KF.2Al(C₂H₅)₃).4 toluene.



Fig. 2. Rotation dependence of current according to the "Mixed Control"-Levich-equation at overpotentials indicated.



Fig. 3. Tafel plot for moderate overpotentials.



Fig. 4. Tafel plot for the aluminum deposition.

for electron transfer kinetics of a metal-ion system with valency z[22] this yields an anodic transfer coefficient of ideally $\alpha = 0.5$ and z = 3. At moderate overvoltages (ie $|\eta| < 0.1$ V, or |j| < 3 mA cm⁻²) the controlling step is charge transfer of three electrons to one aluminum complex. The extrapolation to $\eta = 0$ yields an exchange current density $j_0 = 0.35$ mA cm⁻². An independent evaluation of the charge transfer resistance $d\eta/dj = RT/zFj_0$ gave a $j_0 = 0.4\overline{4} \text{ mA cm}^{-2}$ which is in good agreement with the value above. Going to higher overvoltages (ie $|\eta| > 0.1$ V, or $|j| > 3 \text{ mA cm}^{-2}$) the overall deposition rate is not any more determined by the relatively fast electron transfer. Figure 3 indicates a cathodic current plateau characteristic for a kinetic reaction limited current j, at which the species discharged during electron transfer reaches a steady state concentration near zero. The anodic Tafel region[23]:

$$\eta_{+} = b \log |j_t/p^{0.5}| + b \log |j|, \qquad (3a)$$

$$b = 2.3 (2v \text{ R} T)/(z(p+1)\text{F},$$
 (3b)

can be extrapolated to $j_r/p^{0.5} \cdot p$ Stands for the stoichiometric coefficient of the aluminum complex in the rate determining homogeneous chemical process in the so-called reaction layer; v is the stoichiometric coefficient of the aluminum species in the overall electrode reaction. The denominator of b becomes zpF if the rate-limiting reaction would be heterogeneous[24] which cannot be decided here. The extraordinary high value of the experimental b indicates a high v/p and consequently, a complicated chemical process preceding charge transfer above -0.1 V.

Wave B occurs on top of the j_r plateau, and yields a Tafel behavior between -0.3 and -0.7 V. Shiny microcrystalline deposits of aluminum are formed here. This shows that a further cathodic mechanism occurs at this overvoltage. Since no second current plateau is observed a simple reaction rate limitation cannot serve as an explanation. The b_{\perp} value appears extremely high. Assuming either electron transfer[22] or rather a crystallization rate control by surface with an analogous $b_{-} = 2.3 \text{R} T/(z(1$ diffusion $-\alpha$)F)[25] the anodic transfer coefficient α comes out almost equal 1. This would indicate an extremely asymmetric activation for this high-voltage process. Definite explanations about the mechanisms involved in waves B and C cannot be given at this point.

3.2 Voltage pulse deposition on vitreous carbon

On aluminum substrates, the current response to a potentiostatic pulse decays with time according to the $j vs t^{-0.5}$ law[26] for all values of η till it reaches a steady state level indicating a simple diffusion-controlled process. The early current transients of aluminum deposition on a foreign substrate, *ie* vitreous carbon (Fig. 5), show overvoltage dependent fast initial peaks and successive rising portions up to a time, when the surface is fully covered and behaves as a solid aluminum substrate. This can be treated as processes of nucleation and growth preceding the bulk deposition.

The analysis of these early stages of electrocrystallization by means of a log j vs log t plot in Fig. 6 indicates that there is a transition from a linear j-t to a $j-t^{0.5}$ relationship. The initial j-t portion is in accordance with a peripherally controlled growth of N twodimensional nuclei[27]:

$$j = (2zF \pi Mhk^2/d) N t, \qquad (4)$$

where k is the kinetically controlled growth rate in mol cm² s⁻¹, h the height of the two-dimensional growth center, M and d the molecular weight and the density of aluminum. N stands for the instantaneous number of nuclei on the surface, and the other symbols have their usual significance. One-dimensional needle growth and two-dimensional progressive diffusion controlled growth would also give linear j-t results [28] but appear improbable in this context. In range B at overvoltages less than -0.65 V, crystallization or a chemical process inhibits the rate at low currents and initial short times. Beyond a η -dependent time limit and a certain j the kinetic domain is left and diffusion takes over control of the growth rate (see below).

The slope of the j-t plot in Fig. 5 is strongly η -dependent. We assume that the kinetic rate constant



Fig. 5. Potentiostatic transient for the deposition of aluminum on vitreous carbon at overpotentials indicated.



Fig. 6. $\log j - \log t$ plots for the growth of aluminum nuclei on vitreous carbon (data from Fig. 5). The slopes of the straight line portions are 1 and 0.5.

k in Equation (4) is constant in a first order approximation. The number of two-dimensional nuclei renders itself the potential dependent term. The reversible work of nucleation A_c is mainly a function of η and the boundary free energy [29]:

$$A_{\rm c} = (\pi \rho^2 \bar{A}) / (z F|\eta|), \qquad (5)$$

with \bar{A} the molar area covered by one mole in a monolayer. The number of nuclei formed can be given in the form of a statistic Boltzmann equation:

$$N = N_0 \exp(-A_c/k_B T), \tag{6}$$

 N_0 being the total number of all possible nucleation sites. Therefore N_0 , and with it N, will mainly depend

on the nature of the substrate. The nucleation peak current occurring in the ms-time domain (not well resolved on the scale of Fig. 5) can be regarded as directly proportional to the number of two-dimensional nuclei formed, ie $j \propto N$:

$$\log j = \log z F N_0 - (\pi \rho^2 \bar{A} / z F k_B T) \cdot |\eta|^{-1}, \quad (7)$$

according to Equations (4)-(6), and the assumption k is constant. A plot of the nucleation peak current recorded after 9 ms actually yields a straight line between -0.35 and -0.65 V (Fig. 7). This supports our model of two-dimensional nuclei growing kinetically controlled at their peripheries. Beyond -0.60 V, however, Fig. 7 shows a second linear portion with a greater slope, *ie* nucleation work. A



Fig. 7. Nucleation peak currents vs η^{-1} . Potential dependence of two-dimensional nucleation on vitreous carbon.

mechanistic change has already been indicated around this overvoltage phenomenologically in Figs 1 and 4. Actually, there is strong evidence for co-deposition of aluminum and alkalimetal at these high overvoltages [30]. The slopes of the straight lines in Fig. 7 are determined by the ratio at the molar area covered by one mole in a monolayer, \overline{A} , and the charge z. In the domain $|\eta| > 0.6$ V, where aluminum with z=3 and potassium with z=1 are most probably deposited, this ratio, ie the negative slope, is about 2.6 times greater than for pure aluminum deposits at $|\eta| < 0.6$ V. Though \overline{A} of potassium is greater than of aluminum, the charge z (in the denominator) obviously controls the slopes. The intercept at $\eta^{-1} = 0$ represents a measure of the maximum number of nucleation sites N_0 characteristic of a certain substrate surface. N_0 turns out to be of practical relevance for the adherence and the morphology of a deposit. The second section of the $\log j$ vs $\log t$ plot in Fig. 6 indicates a $j-t^{0.5}$ relationship. An evaluation of this situation can be presented by the model of material transport to already formed three-dimensional nuclei by planar diffusion[31]:

$$j = (8zFM^2D^{1.5}c^3)/(d^2\pi^{0.5})Nt^{0.5}.$$
 (8)

The experimental $j-t^{0.5}$ plot actually yields a straight line (Fig. 8). An alternative equation was proposed for hemispherical diffusion instead of linear which differs mainly by the exponents of D and c[32]. Progressive nucleation would be recognized by a $t^{1.5}$ dependence[28] which was not fulfilled here. A final decision what diffusion mode applies is not possible at this point. Finally, an overlap of the individual diffusion fields of the nuclei would render a mixed t-dependence differing from $t^{0.5}$ [33], and could not be observed in the present case. These findings are in accord with the above rotating disk results that at steady state diffusion dominates the rate.

The assumption of diffusion controlled growth requires that the j vs $t^{0.5}$ gradients should be independent of potential when N were constant. It can be seen from Fig. 8 that in this system not only the slopes but also the intercepts at j=0, standing for an initiation time τ , markedly depend on the applied potential. It



Fig. 8. $j vs t^{0.5}$ plot for the growth of aluminum nuclei on vitreous carbon at overpotentials indicated (data from Fig. 5).



Fig. 9. $j \cdot t^{-0.5} vs \eta^{-2}$. Potential dependence of three-dimensional nucleation on vitreous carbon.

can be shown that N determines the slope in analogy to the two-dimensional case. The reversible work of three-dimensional nucleation is[29]:

$$A_{\rm c} = (16\pi\sigma^3 \bar{V}) / (3z^2 F^2 \eta^2). \tag{9}$$

Here σ is the surface free energy and \bar{V} the molar volume. With this and the Boltzmann relationship of

Equation (6) the surface concentration of nuclei is N proportional to η^{-2} (first approximation). The slope of Equation (8), j vs $t^{0.5}$, is a function of N, and we therefore get the proportionality:

$$\log jt^{-0.5} = \operatorname{const.} \log N_{\rm o} - \operatorname{const.} \eta^{-2}.$$
(10)

The straight character of Fig. 9 supports the above view of a potential dependent three-dimensional nucleation. The intercept at $\eta^{-2} = 0$ represents a measure of the maximum number of nucleation sites N_o characteristic for the substrate.

4. SUMMARY

In the electrodeposition of aluminum from $KF.2Al(C_2H_5)_3$ onto conducting substrates, at least five different rate limiting mechanisms could be detected. Depending on the applied overvoltage, charge transfer, material transport, slow homogeneous chemical reactions and crystallization steps play decisive roles. Stationary polarizations over -0.1 V generally generated a material transport limitation. By means of rotating electrodes and pulse techniques the diffusion rate was controlled to uncover kinetic electron transfer and reaction currents.

At low overvoltage near the equilibrium of the aluminum electrode the transfer of three electrons to an aluminum complex-species determines the rate. The exchange current of about 0.4 mA cm⁻² is comparable to aqueous plating baths as, eq, of zinc.

Extending the overvoltage to -0.1 until -0.3 V, however, a chemical dissociation process preceding charge transfer becomes the slowest step. The current is limited to a value around -5 mA cm⁻².

In the range of -0.3 up to -0.7 V another deposition mechanism occurs in form of a flat kinetic current wave below ca - 20 mA cm⁻². The unusual kinetic parameters point onto possible slow chemical reactions and/or surface diffusion, *ie* crystallization.

Above an overvoltage of ca - 0.7 V the current exhibits a strong further wave strongly influenced by mass transport from the bulk electrolyte. Its mechanistic nature is still not identified.

The voltage pulse deposition of aluminum on a foreign substrate, here vitreous carbon, gave a detailed insight into the initial steps of electrocrystallization which are nucleation and growth. We detected a peripheral reaction controlled growth of instantaneously formed two-dimensional plates, at short pulse times and low overvoltage, on top of plates so as to produce three-dimensional nuclei at longer pulse durations and higher overvoltages which then grow by a transport limited mechanism.

Growth rates of nuclei are a function of the number of the instantaneously formed nuclei N. This is determined by the substrate dependent maximum number of nucleation sites N_{o} , and the reversible work of nucleation which exhibits an exponential dependence on the first or second power of overvoltage. Thus, we could describe a method of comparing substrates with respect to their particular density of nucleation sites which represents the fundamental criterion for the coating adhesion and morphology.

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