Electrochemical determination of current efficiency for aluminium deposition on solid substrates from cryolitic melts

J. M. TELLENBACH, D. LANDOLT

Materials Department, Swiss Federal Institute of Technology, CH-1007 Lausanne, Switzerland

A potentiostatic double pulse method has been developed for the measurement of current efficiency of aluminium deposition from cryolitic melts on solid substrates. The method is based on the measurement of the ratio of anodic to cathodic charge. Its application is at present limited to laboratory cells. The method described is useful for the study of the influence of different parameters such as electrolyte composition, temperature or convection conditions on current efficiency for aluminium deposition.

1. Introduction

Aluminium deposited on solid substrates such as tungsten and titanium diboride dissolves spontaneously in cryolitic melts [1–4]. The dissolution process is of a physical rather than electrochemical nature and the rate of dissolution is controlled by mass transport of dissolved metal from the electrode into the bulk electrolyte [1]. According to the physical dissolution model (PDM) the rate of aluminium loss does not depend on the prevailing electrode potential and, therefore, is the same during cathodic deposition, at open circuit and during anodic oxidation. This suggests the possibility of using potentiostatic deposition–reoxidation for the study of the rate of the cathodic loss reactions and of current efficiency. Previously [1–3] galvanostatic pulses were used for this purpose. Anodic oxidation at constant current, however, leads to a potential jump and to attack of the substrate material once the aluminium has disappeared. For this reason, the galvanostatic method is essentially limited to open circuit corrosion studies but these do not give current efficiency directly [1]. In the present paper a potentiostatic double pulse method is described which allows one to reoxidize the cathodically deposited aluminium at a set rate without attacking the substrate. The technique is used for the determination of current efficiency for cathodic deposition of aluminium on tungsten and titanium boride substrates.

2. Experimental details

The tubular furnace used in the present study has been described previously [3, 4]. The electrolyte, handpicked Greenland cryolite, is contained in a pyrolitic boron nitride crucible of 45 mm diameter. The molten cryolite is held at 1020° C in an Ar atmosphere. The working electrode is either a vertical cylindrical rod immersed to a depth of 10 mm or a flat disk facing downwards, press-fitted into a BN insulation [3]. A nickel/cryolite

reference electrode contained in a hot pressed BN tube is used. The counter electrode is made of a 1.5 mm dia. tungsten rod placed at a distance of 25 mm.

Figure 1 illustrates the potentiostatic double pulse technique employed in the present study. At the beginning of an experiment, a potential E_1 slightly positive to the open circuit potential, E_{oc}, of the substrate is imposed in such a way that the anodic current density is 50–$100 \, \mu A \, cm^{-2}$. After reaching steady-state conditions a cathodic potential, E_2, is applied for a duration of 5–20 s. Aluminium deposition takes place at current densities of 0.1–$10 \, A \, cm^{-2}$. The potential is then switched to a value E_3 and held for a time of 5–20 s, typically. The potential E_3 is chosen between E_2 and E_{oc} in such a way that the cathodically deposited aluminium undergoes anodic reoxidation at a rate which depends on the value of E_3. After a preset time the potential is switched back to E_1. The position of E_1, E_2, E_3 with respect to the current–voltage behavior of the electrolyte is illustrated by the cyclic voltammogram shown in the insert of Fig. 1. Also shown in the figure is the shape of the current transients (schematic) observed at E_2 and E_3. By integration, the cathodic

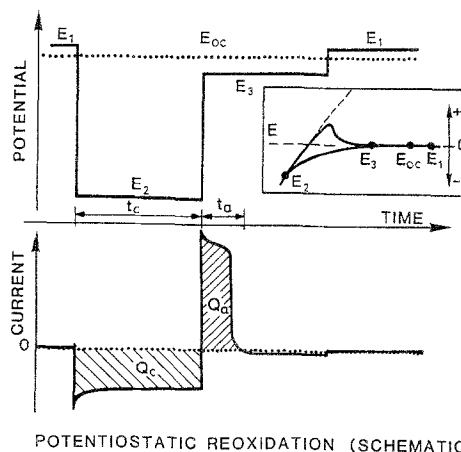POTENTIOSTATIC REOXIDATION (SCHEMATIC)

Fig. 1. Potentiostatic double pulse technique and single sweep voltammogram in molten cryolite.
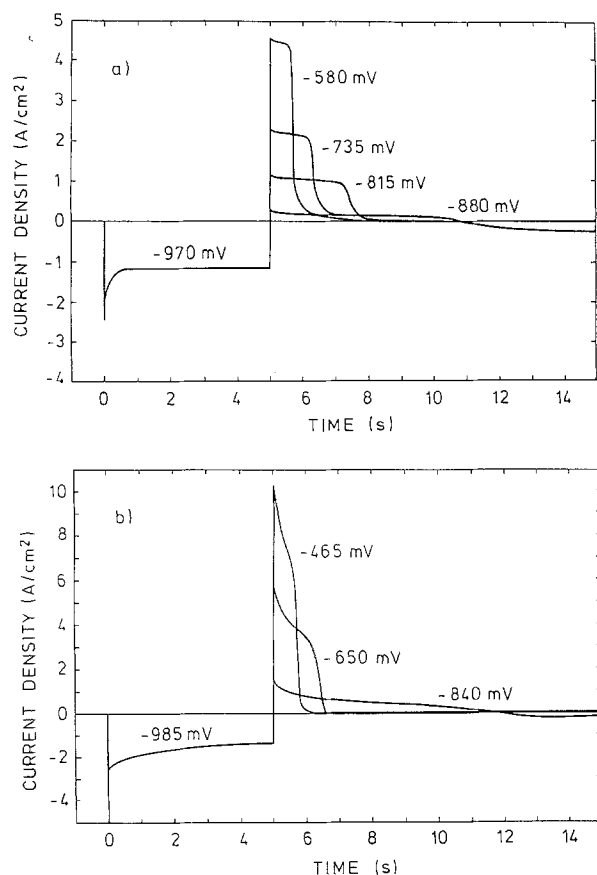
Fig. 2. Current transients measured on (a) a W rod and (b) a W disk, at different reoxidation potentials E_3.
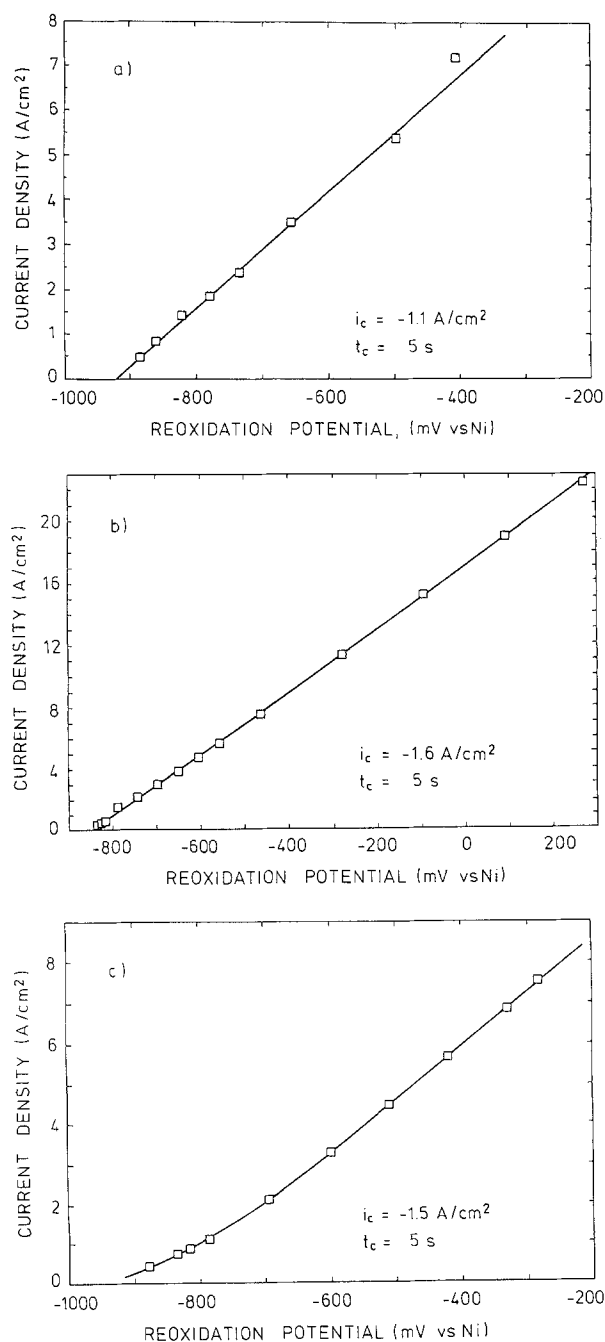

Fig. 3. Measured anodic polarization curves (mean value of plateau current) during time t_a for aluminium oxidation on (a) a W rod, (b) a W disk and (c) a TiB$_2$ rod.

and anodic charge Q_c and Q_a, respectively, can be calculated. The anodic current density drops to essentially zero long before the potential E_3 is switched back to E_1 because all deposited aluminium has reacted.

In typical experiments, the influence of a given variable such as E_2, E_3, temperature etc. on the charge ratio Q_a/Q_c is determined. The experimental set-up consists of a potentiostat (Amel 551) driven by a programmable function generator (AMEL 568). Two electrometers (Keithley 616) serve as interface for the measurement of current and potential which are recorded on a digital oscilloscope (Nicolet 4094). Both the digital oscilloscope and the function generator are interfaced with a computer (HP 9836U). Data are plotted on a digital plotter (HP 7475A). More details are given elsewhere [4].

3. Results

In Fig. 2 current transients measured on a tungsten rod (a) and a tungsten disk (b) at different values of the reoxidation potential, E_3, are shown. The cathodic current density is approximately $1.1 \, \mathrm{A \, cm^{-2}}$ (a) and $1.6 \, \mathrm{A \, cm^{-2}}$ (b), respectively; the cathodic deposition time is $t_c = 5 \, \mathrm{s}$ in both cases. The data illustrate the excellent reproducibility of the cathodic current transients. They also show that the value of the reoxidation current density i_a and the reoxidation time t_a depend on the applied value of the reoxidation potential E_3. The shape of the current transients is similar on the rod and on the disk electrode but the current plateau

is more pronounced on the former. This could possibly be due to a more uniform current distribution or to a lower free convection rate on the rod. Figure 3 shows the variation of the measured plateau current (mean value) with applied potential E_3 for the two electrode geometries. The largely linear behaviour suggests ohmic control. Indeed, at the high current densities prevailing in these experiments, the potential drop in the electrolyte between reference electrode and working electrode is much larger than the working electrode potential. The present experiments, therefore, are not truly potentiostatic because the sum of ohmic drops and working electrode potential rather than the working electrode potential is kept constant. From a practical point of view, the prevailing ohmic control is not an inconvenience, however, because, as will be shown
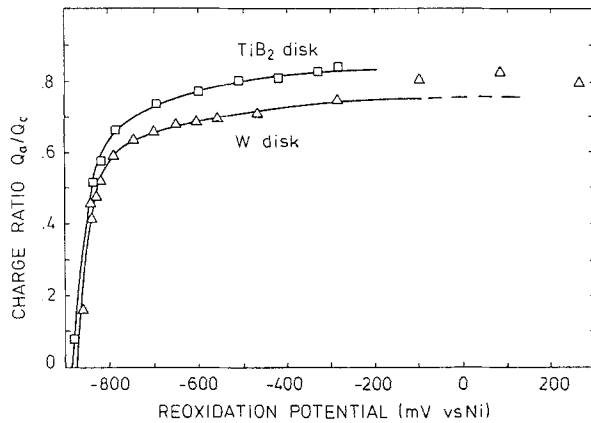
Fig. 4. Charge ratio, Q_a/Q_c, as a function of the reoxidation potential, E_3, measured on stationary W and TiB$_2$ disk electrodes.

Fig. 5. Charge ratio, Q_a/Q_c, as a function of the mean cathodic current density measured on a W rod and on a stationary W disk. $E_3 = 50 \, \text{mV}$.

below, the current density rather than the potential determines the cathodic current efficiency. In an ohmically controlled system the current density varies less with potential than in a system controlled by cathodic overvoltage well below the limiting current, and therefore is easier to maintain. From the data of Fig. 3 it follows that the ohmic potential drop is slightly higher with the disk than with the rod electrode. Because of a larger surface area, the maximum current density that could be reached with the potentiostat used was lower on the rod than on the disk.

In Fig. 4 the measured charge ratio Q_a/Q_c for disk electrodes made of tungsten and of TiB$_2$ is shown as a function of the applied reoxidation potential E_3. In these experiments $i_c = 1.6 \, \text{A cm}^{-2}$, $t_c = 5 \, \text{s}$, $T = 1020°\text{C}$. The data show that at a potential $E_3 < 800 \, \text{mV}$ vs Ni/cryolite the ratio Q_a/Q_c rapidly increases with E_3 then tends towards a limiting value. The measured Q_a/Q_c ratios at the most anodic potentials seem systematically too high. The reason for this is not known but could be related to substrate oxidation or to less precision in the measurement due to the extreme anodic current density values under these conditions. In spite of this uncertainty both W and TiB$_2$ in Fig. 4 clearly exhibit a limiting behaviour at high anodic potentials. This suggests that the potentiostatic double pulse method can be used for measuring the cathodic current efficiency for aluminium deposition (see below).

In the following experiments, anodic oxidation is always carried out in the limiting region, at $E_3 = -50 \, \text{mV}$ on tungsten and $-400 \, \text{mV}$ on TiB$_2$. The lower value on TiB$_2$ is chosen to avoid any danger of anodic oxidation of the substrate [2, 4].

The influence of the applied potential E_2 on Q_a/Q_c is shown in Fig. 5 for a tungsten rod and disk electrode, respectively. The current density i_c, rather than E_2, is plotted on the abscissa (cf. Fig. 3). The deposition time $t_c = 5 \, \text{s}$ of the experiments is sufficiently long for Q_a/Q_c to be independent of t_c (see below). The data show that at low i_c the value of Q_a/Q_c is higher on the rod than on the disk. This observation is consistent with previous observations that the rate of aluminium loss is higher on a disk than on a rod because of more intense free convection [4]. To study the influence of
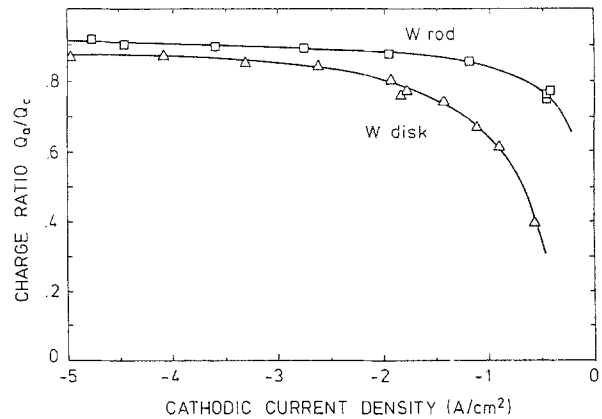
convection on Q_a/Q_c a rotating TiB$_2$ disk electrode, described elsewhere in detail [3], was employed. Data obtained for $i_c \approx 3.5 \, \text{A cm}^{-2}$, $t_c = 5 \, \text{s}$ are shown in Fig. 6. A slight decrease of Q_a/Q_c with rotation rate is observed but the effect is relatively small.

A few experiments were performed in an electrolyte of a cryolite ratio CR $= 2.7$ containing 6% CaF$_2$ and 4% Al$_2$O$_3$, resembling the composition used industrially. The temperature was varied between 925 and 966°C. Figure 7 shows the influence of deposition time on the measured Q_a/Q_c ratio for a cathodic current density of 0.9–1 A cm^{-2} at 966°C. For 5 s $\leqslant t_c \leqslant 20$ s the measured Q_a/Q_c is independent of t_c and hence of the amount of deposited aluminium. This confirms the validity of the method. The slightly lower values of Q_a/Q_c at $t < 5$ s are attributed to the fact that upon switching on the current the dissolved metal concentration at the cathode must build up first before deposition sets in. Figure 8 shows limiting values of Q_a/Q_c measured in the same electrolyte at different cathodic current densities and different temperatures. With increasing i_c the value of Q_a/Q_c increases. Decreasing the temperature also increases Q_a/Q_c.

4. Discussion

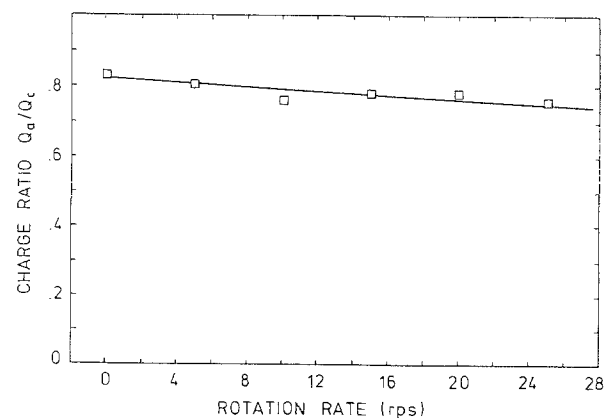The rate of aluminium loss at the cathode due to

Fig. 6. Charge ratio, Q_a/Q_c, as a function of rotation rate measured on a TiB$_2$ disk. $E_3 = -400 \, \text{mV}$, $i_c \approx 3.5 \, \text{A cm}^{-2}$, $t_c = 5 \, \text{s}$.
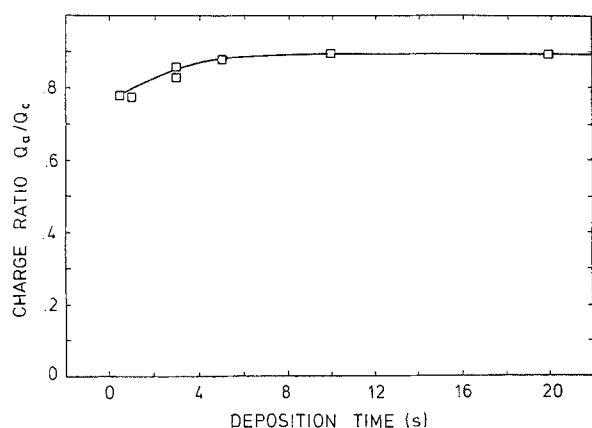
Fig. 7. Charge ratio, Q_a/Q_c, as a function of the deposition time measured on W rod in an industrial electrolyte (CR = 2.7, 6% CaF_2, 4% Al_2O_3) at 966° C.

dissolution into the electrolyte is [1]

$$N_M = D_M \frac{(C_s - C_b)}{\delta} \qquad (1)$$

where N_M is the flux of dissolved aluminium, D_M is the diffusion coefficient, C_s and C_b are the concentration of dissolved aluminium at the electrode surface and in the bulk, respectively. In the present experiments $C_b = 0$. The thickness, δ, of the diffusion layer depends on convection conditions.

The loss current density, $i_{loss} = 3FN_M$, represents that part of the cathodic current density which is used for production of aluminium 'lost' into the bulk. Similarly, the loss charge, Q_{loss}, is defined as $Q_{loss} = \int i_{loss} \, dt$. The total charge, Q_c, passed during the cathodic cycle (E_2) is then

$$Q_c = Q_{dep} + Q_{loss,c} \qquad (2)$$

where Q_{dep} is the charge corresponding to the aluminium that is actually present on the cathode at time t_c and $Q_{loss,c} = \int_0^{t_c} i_{loss,c} \, dt$ is the charge corresponding to the aluminium lost during the cathodic cycle. The current efficiency for aluminium deposition, θ_c, is given by Equation 3

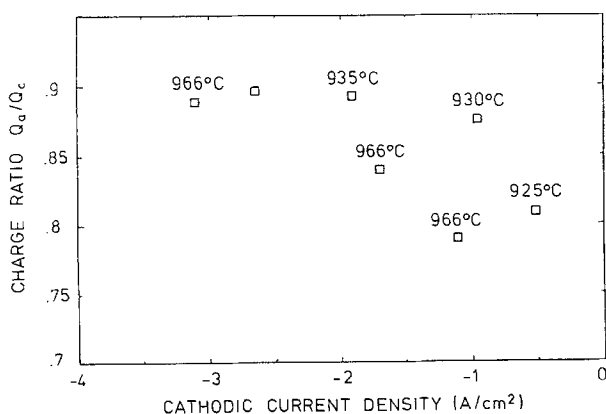$$\theta_c = \frac{Q_{dep}}{Q_c} \qquad (3)$$

Fig. 8. Charge ratio, Q_a/Q_c, for different cathodic current densities and different temperatures. Stationary W disk, same electrolyte as for Fig. 7.

During the anodic pulse (E_3) a charge Q_a is passed. Let us assume that oxidation of aluminium is the only electrochemical reaction but that physical dissolution of aluminium takes place during the anodic cycle. The corresponding loss current density is $i_{loss,a}$ and the loss charge is $Q_{loss,a} = \int_{t_c}^{t_c+t_a} i_{loss,a} \, dt$. One gets for the anodic charge:

$$Q_a = Q_{dep} - Q_{loss,a} \qquad (4)$$

For the charge ratio Q_a/Q_c it follows

$$\frac{Q_a}{Q_c} = \theta_c - \frac{Q_{loss,a}}{Q_c} \qquad (5)$$

As a good approximation, one may write $Q_{loss,a} \approx i_{loss,a}t_a$ and $Q_a \approx i_a t_a$. Eliminating $Q_{loss,a}$ from Equation 5 one obtains Equation 6

$$\frac{Q_a}{Q_c} = \theta_c \left(\frac{i_a}{i_a + i_{loss,a}} \right) \qquad (6)$$

It follows that the ratio Q_a/Q_c is equal to θ_c if $i_a \gg i_{loss,a}$. The described behaviour is in good agreement with the data of Fig. 4 which show that, with increasing E_3, i.e. increasing value of i_a (Fig. 3), the ratio Q_a/Q_c tends towards an asymptotic value.

In the original PDM [1] the rate of aluminium loss is assumed to be independent of potential, $i_{loss,c} = i_{loss,a} = i_{loss}$. Recently, it has been shown [4] that under certain conditions $i_{loss,c}$ may vary with the cathodic current density due to concentration changes of ionic species within the cathodic diffusion layer. From the derivation given here it follows that Equation 6 is also applicable in such a case.

The data of Figs 7 and 8 show that the potentiostatic double pulse method is applicable in industrial electrolytes and should, therefore, be useful for laboratory investigations of the influence of melt composition on current efficiency. The data of Fig. 8 suggest that the current efficiency increases with increasing cathodic current density and with decreasing temperature. This is consistent with industrial experience [5] but the absolute values in Fig. 8 are lower than those typically found in industrial cells.

The difference is attributed to the fact that the bulk electrolyte in industrial cells contains dissolved aluminium in a concentration which depends, among other things, on the rate of consumption of dissolved aluminium by anodic oxidation and by reaction with CO_2 [5, 6]. According to Equation 1 the rate of aluminium dissolution at the cathode is proportional to $C_s - C_b$. In the present experiments, contrary to industrial conditions, $C_b = 0$, i.e. the rate of aluminium dissolution should be higher. A further difference between laboratory cells and industrial cells concerns convection. According to Equation 1 increasing the convection rate increases the rate of aluminium dissolution, i.e. decreases current efficiency. In industrial cells both the dissolved aluminium bulk concentration and the convection conditions at the cathode are not well known [5, 7] and, therefore, it is not surprising that the absolute value of current efficiency differs between industrial and laboratory cells. On the

other hand, laboratory cells can be used to evaluate, on a relative basis, the influence of operational parameters such as electrolyte composition and temperature on current efficiency. For such studies the double pulse method for the determination of current efficiency described in the present paper is faster and simpler to use than methods based on chemical analysis.

Acknowledgements

References

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