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# Influence of the substrate on the rate of aluminium loss in molten cryolite

J. M. TELLENBACH, D. LANDOLT

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

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The rate of redissolution of aluminium cathodically deposited from cryolitic melts on solid substrates made of tungsten or titanium diboride has been investigated. Results show that tungsten and titanium diboride lead to similar rates of aluminium loss but surface preparation is an important variable. The presence of aluminium in the bulk electrolyte reduces the rate of the loss reaction.

## 1. Introduction

The current efficiency of Hall Heroult aluminium cells is limited by recombination reactions between anodic and cathodic reaction products [1–3]. Different loss mechanisms have been discussed in the literature [4] but the rate determining step is not known with certainty. An important reaction step is dissolution of deposited aluminium into the electrolyte. According to Duruz and Landolt [5] the dissolution rate of aluminium in cryolitic melts is mass transport controlled and independent of potential (or current density). Within the parameter range studied, measurements of the open circuit corrosion rate and anodic stripping experiments on tungsten agreed well with the physical dissolution model (PDM) proposed by these authors [5]. On the other hand, it is known that tungsten can form alloys with deposited aluminium [6–8], the thickness of the alloy layer increasing with the square root of time [9]. To substantiate the PDM, experiments with an inert substrate such as $TiB_2$ are needed. The aim of the present paper is the investigation of the role of the substrate on the rate of aluminium loss at solid cathodes.

## 2. Experimental

The cell assembly was placed in a 600 mm long, 70 mm diameter alumina tube protected on the inside by a nickel sheath and placed in a vertical furnace with Tantal wire resistance heating. The upper and lower ends of the furnace were closed with water cooled brass covers containing fittings for fixing the electrodes and thermocouples. Radiation losses were minimized by nickel plates placed above and below the crucible. The furnace could be evacuated to $10^{-2}$ Torr and refilled with argon. A more detailed description is given elsewhere [5, 9]. The electrolyte was hand picked Greenland cryolite ($Na_3AlF_6$) [5] dried in the furnace at 250° C and $8 \times 10^{-2}$ Torr for 12 h. Argon was then admitted providing a continuous flow of $0.2\ \mathrm{l\,min^{-1}}$ during the experiments. Before starting an experiment the melt was maintained at 1020° C for 2 h. A $50\ \mathrm{cm^3}$ pyrolitic boron nitride (BN) crucible was employed. The temperature was measured with a Pt-Pt10%Rd thermocouple placed at the base (outside) of the crucible.

The working electrode made of tungsten (> 99% Elektrometall AG) or titanium diboride (Alusuisse, porosity 1.3%) was in the form of a rod immersed in the melt to a predetermined depth or in the form of a disk surrounded by a BN insulation. The electrodes were used either in the 'as-received' condition or after mechanical polishing. Table 1 summarizes the characteristics of the different electrodes and the experimental parameter range used in this study.

The counter electrode was a tungsten wire of 1.5 mm diameter and $1.6\ \mathrm{cm^2}$ active surface. A high purity nickel wire (99.995%) dipping in cryolite contained in a hot-pressed boron nitride crucible with a small hole was used as reference electrode. The potential of this electrode was stable within ± 10 mV during a typical experiment of 2–4 h [10]. The three electrodes were placed in the cell in the form of an equilateral triangle at a distance of approx. 25 mm from each other.

A potentiostat (Amel 551) with a function generator (AMEL 568 or 566) was employed. The potential and/or current were monitored with an electrometer (Keithley 616) connected to an X-Y recorder or digital oscilloscope (Nicolet 4094). In some experiments a HP 9836U computer was used for data acquisition. More details of the experimental set-up are given elsewhere [9]. In a typical experiment aluminium was deposited at constant current and the potential decay transient at open circuit was monitored. From the measured decay time the rate of aluminium loss was calculated as described below.

## 3. Results and discussion

In Fig. 1 potentiodynamic current voltage curves measured on $TiB_2$, W and Au (1 mm diameter wire) are shown. Among the three electrodes Au is the most stable, anodically. On the other hand, $TiB_2$ is easily oxidized at potentials $\geqslant -220$ mV with respect to the nickel reference electrode. Cathodically, the W and $TiB_2$ electrodes behave similarly but residual currents

*Table 1. Experimental parameters*

| *Electrode* | | | | | *Parameter range* | |
|---|---|---|---|---|---|---|
| *Material* | *Shape* | *Surface state* | *Diameter* (mm) | *Geometrical area* ($cm^2$) | *Applied current density* ($mA\,cm^{-2}$) | *Deposition time* (s) |
| W | rod | as-received | 2 | 0.66 | 75–600 | 2 |
| W | rod | mech. polished<br>600 grit SiC | 2 | 0.66 | 150–900 | 2–5 |
| $TiB_2$ | rod | mech. polished<br>1/4 μm diam. | 3 | 0.96–1.0 | 200–800 | 1–5 |
| W | disk (BN insulation) | mech. polished | 2.5 | 0.05 | 200–2000 | 10 |

on $TiB_2$ are higher. The cathodic decomposition voltage of cryolite on Au is significantly lower than on the other materials because of alloying [6, 8]. In Fig. 2 cyclic voltammograms measured on the three electrode materials and on Mo at potentials cathodic to the open circuit potential are shown (the open circuit potentials were 50–80 mV for W, Mo and Au, $-220$ mV for $TiB_2$). For all electrode materials the cyclic voltammograms show a distinct oxidation peak due to reoxidation of deposited aluminium [5]. Tungsten and titanium diboride were chosen for further study.

To study the rate of aluminium loss aluminium was deposited at constant current followed by open-circuit corrosion. The potential transient was monitored as shown in Fig. 3 which represents experiments performed at a cathodic current density of 0.33, 0.63 and 0.88 $A\,cm^{-2}$, respectively, and a deposition time of $t_c = 2$ s. Upon current switch-off a potential plateau was reached rapidly. After a time $t_0$ the deposited aluminium had dissolved and the potential abruptly changed to a value of $\sim -200$ mV against Ni.

According to the PDM the rate of aluminium dissolution, $N_M$, is given by equation (1), where $D$ is the diffusion coefficient of dissolved aluminium, $C_s$ and $C_b$ are the concentrations of dissolved aluminium at the surface and in the bulk, respectively, and $\delta$ is the diffusion layer thickness, the value of which depends on convection conditions.

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

Aluminium dissolution in cryolitic melts yields a number of metallic and subvalent equilibrium species of aluminium and sodium [2]. The dissolved aluminium concentration designates the equivalent amount of metallic aluminium which corresponds to all these species. The diffusion coefficient, $D$, and the diffusion layer thickness $\delta$ in equation (1), therefore, represent an average for the different species.

It is convenient to define a loss current density $i_{loss}$:

$$i_{loss} = 3FN_M \qquad (2)$$

The applied cathodic current density during aluminium deposition, $i_c$, is then the sum of the net deposition current density $i_{dep}$ and the loss current density, $i_{loss}$: $i_c = i_{dep} + i_{loss}$. Assuming in a first approximation that $\delta$ is constant for a given experiment and that $C_s$ is also a constant one can calculate $i_{loss}$ from the measured potential transients:

$$i_{loss} = \frac{Q_c}{t_{diss}A} \qquad (3)$$

Here $Q_c$ is the cathodic charge passed during the experiment, and $A$ is the electrode area. The dissolution time $t_{diss}$ is the sum of the cathodic deposition time $t_c$ and the potential decay time $t_0$.

$$t_{diss} = t_c + t_0 \qquad (4)$$

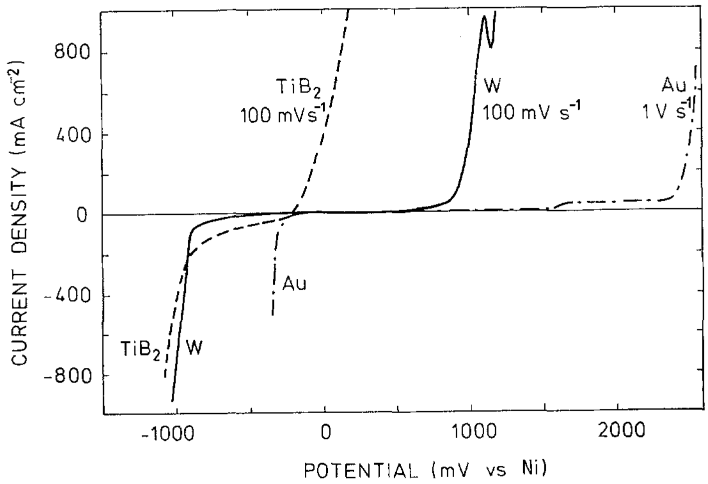

Fig. 1. Potentiodynamic polarization curves on different substrates in pure cryolite at 1020° C.

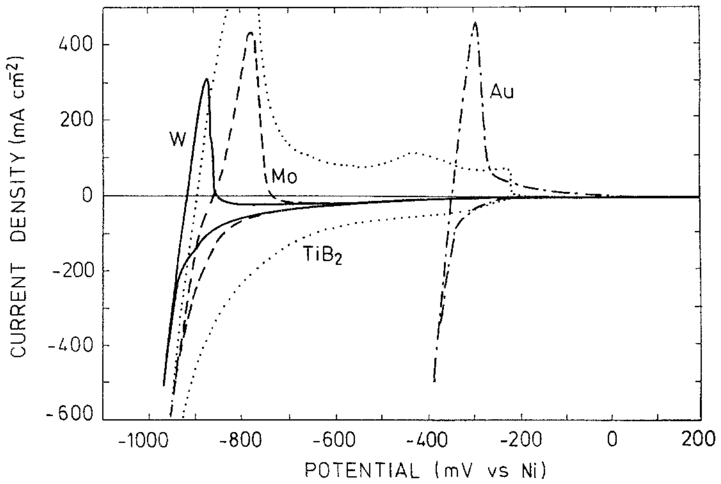

Fig. 2. Cyclic voltammograms on different substrates in cryolite at 1020° C.

Equation (4) is based on the hypothesis that Al dissolves at the same rate during cathodic deposition and at open circuit [5]. Values of $i_{\mathrm{loss}}$ calculated by equation (3) from a large number of experiments performed on rod shaped electrodes of W and $TiB_2$ at different current densities and deposition times are plotted in Fig. 4 as a function of the cathodic charge $Q_c$. For sufficiently large values of $Q_c$ the loss rate becomes independent of cathodic charge and hence of the amount of Al deposited, in good agreement with the PDM. For small $Q_c$ the apparent loss rate increases. The behaviour is attributed to the fact that during an initial period after the cathodic current is switched on, no deposition occurs because the Al activity at the cathode must build up first [9]. The calculated loss rate, therefore, is independent of $Q_c$ only if the initial period is small compared to $t_c$ while at short times (small $Q_c$) it is higher. From the data of Fig. 4 it follows that the surface preparation of the cathode plays a crucial role. On as-received tungsten higher $Q_c$ values are needed than on polished tungsten to reach a constant $i_{\mathrm{loss}}$ and the absolute value of $i_{\mathrm{loss}}$ is larger. This behaviour is due to the larger surface roughness of the as-received sample. Because of the resulting larger real surface area the real cathodic current density is lower and at the same time the rate of mass transport of dissolved metal is higher. (The geometrical surface area A in these experiments does not vary much, *cf.* Table 1.) The data of Fig. 3 show that $i_{\mathrm{loss}}$ on $TiB_2$ lies between the values obtained for the two different types of tungsten. This indicates that the electrode material is less critical than the surface preparation and hence the rate of dissolution of aluminium is not affected significantly by alloy formation with tungsten. The absolute values of $i_{\mathrm{loss}}$ for as-received tungsten agree well with those of reference [5] confirming the validity of the experimental technique used.

According to equation (1) the presence of dissolved aluminium in the bulk electrolyte ($C_b \neq 0$) should decrease the rate of aluminium loss at the cathode. To study this effect a number of experiments were performed in which metallic aluminium was added to the electrolyte in amounts exceeding that theoretically needed for saturation of the melt (the saturation concentration of dissolved aluminium is of the order of 0.1 wt% [2]). In a first series of experiments a high purity (99.999%) aluminium wire of 1 mm diameter was cut into small pieces and added to the melt, the added weight corresponding to 0.4 wt% of the melt. Rod electrodes made of tungsten and $TiB_2$ were employed as cathodes. Obtained results given elsewhere [9] were inconclusive, i.e. the value of $i_{\mathrm{loss}}$ was the same or only slightly lower after addition of aluminium. Unfortunately, with the present set-up the concentration of dissolved aluminium in the bulk could not be measured and it was, therefore, considered possible that the melt did not contain sufficient

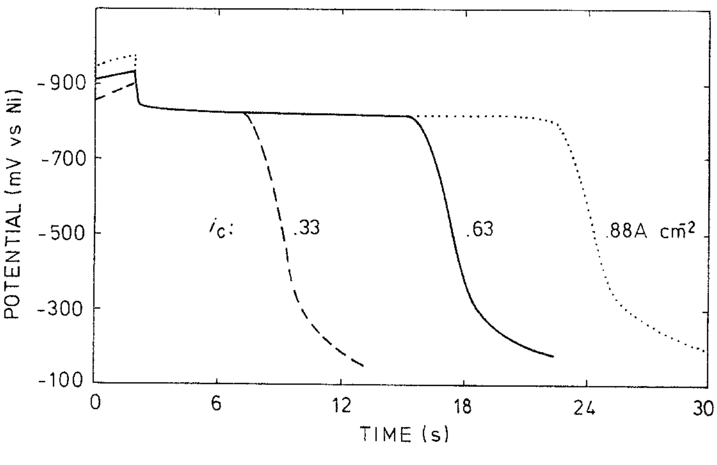

Fig. 3. Potential transients measured during galvanostatic deposition of Al on W electrodes followed by open-circuit dissolution in cryolite at 1018° C. $A = 0.33\,\mathrm{cm}^2$.

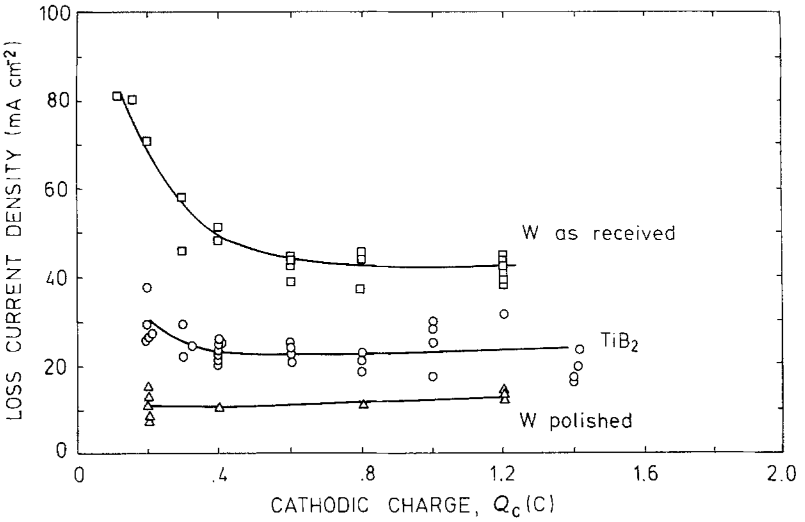

Fig. 4. Loss current densities $i_{\text{loss}}$ for different substrates in cryolite at 1020° C. $A_W \simeq 0.66\,\text{cm}^2$, $A_{\text{TiB}_2} \simeq 1\,\text{cm}^2$.

dissolved aluminium to give a measurable effect. Indeed, it is known that evaporation losses may occur [2] and that dissolution of metallic aluminium added to the melt may be slow [11, 12]. The experiments, therefore, were repeated with a larger amount of aluminium wire added (1.6 wt%) and using cryolite saturated with $Al_2O_3$ to reduce the vapour pressure of dissolved aluminium [2]. Unfortunately, formation of a grey film of metallic appearance was observed on the surface of the electrolyte which prevented meaningful measurements on the rod electrodes. For this reason, a downward facing stationary 2.5 mm diameter disk of W embedded in a BN insolation (HBR UCAR, diameter 10 mm, height 1.5 mm) was used as cathode instead of the rod. The counter electrode was made of carbon. Results obtained with this electrode arrangement in $Al_2O_3$ saturated cryolite before and after addition of aluminium (1.6%) are given in Fig. 5. In the presence of dissolved aluminium in the bulk they show a significant decrease in the measured loss current density, in qualitative agreement with the PDM. On the other hand, according to equation (1) for a saturated solution $i_{\text{loss}}$ should be zero. The finite $i_{\text{loss}}$ values observed in Fig. 5, therefore, suggest that the electrolyte in the present experiments was not saturated. An interesting discussion of problems related to the preparation of solutions of dissolved aluminium in cryolitic melts has recently been given by Odegard [12]. In view of these problems, the relatively high loss current densities observed in the presence of dissolved aluminium in Fig. 5 are perhaps not unexpected. A finite loss current could also be explained by a higher ratio $NaF/AlF_3$ (and hence a higher aluminium solubility) at the cathode surface due to concentration polarization [12–14] or by electronic conductivity resulting from the presence of dissolved aluminium [2]. However, both of these effects are considered not to be of importance here [15].

The loss current densities in the absence of dissolved aluminium given in Fig. 5 are much higher than those shown in Fig. 4 for similar experimental conditions. The reason for this discrepancy is not the presence of $Al_2O_3$ but the different electrode geometry as was confirmed by a large number of experiments performed with different electrode geometries under free convection conditions [9]. A quantitative interpretation of the effects described was not attempted because under the present conditions free convection mass transport depends on ill-defined thermal gradients as well as on concentration gradients and, therefore, no theoretical mass transport correlations are available.

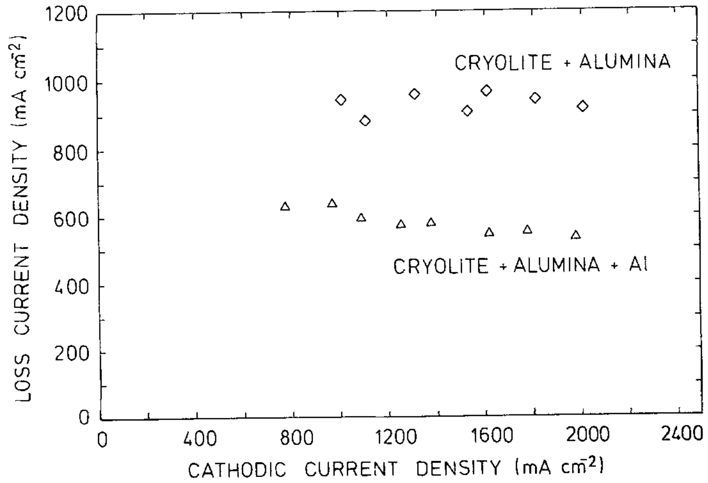

Fig. 5. Influence of dissolved aluminium on loss current density. W disk electrode, cryolite saturated with $Al_2O_3$ at 1020° C.

## 4. Conclusions

The rate of aluminium loss during cathodic deposition from cryolite under free convection conditions does not markedly differ between tungsten and titanium diboride substrates but it is strongly dependent on surface roughness and electrode geometry. The presence of dissolved aluminium in the bulk electrolyte reduces the rate of aluminium loss from the cathode. The present experiments are in qualitative agreement with the physical dissolution model.

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