

Electrochemical deposition of aluminium on tungsten in cryolite based melts

J. J. DURUZ*, D. LANDOLT

Materials Department, Swiss Federal Institute of Technology, Lausanne, Switzerland

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Aluminium deposition and redissolution on tungsten electrodes in cryolite melts of different NaF/AlF₃ ratios have been investigated by potential sweep and galvanostatic techniques. The amount of charge necessary for anodic reoxidation of deposited aluminium was determined as well as the rate of spontaneous corrosion. The qualitative results obtained can be interpreted by assuming a mass transport controlled loss reaction involving metal dissolution in the melt.

1. Introduction

The current efficiency in Hall-Heroult aluminium cells is limited by recombination reactions between cathodically produced metal and anodically produced CO₂ [1, 2]. The recombination rate is dependent on cell geometry and on prevailing convection conditions and it involves metallic or subvalent species dissolved in the melt [3]. To identify the rate limiting steps of these reactions, a better understanding of cathodic reaction mechanisms is needed. An interesting study of cathode phenomena in aluminium electrolysis has been published by Thonstad and Rolseth [4] who showed that concentration polarization is the dominating factor determining overvoltage at the cathode. The authors pointed out that the concentration of ionic species near the cathode may substantially differ from that in the bulk. Different diffusional reaction schemes were also considered by Del Campo *et al.* [5] who used an aluminium coated platinum rotating disk electrode. Previous experiments performed in our laboratory have shown that solid tungsten electrodes can be used advantageously for reversibly depositing and redissolving aluminium from fluoride melts [6]. Although tungsten has a finite solubility in liquid aluminium [7] and alloy formation has been observed [6, 8], reproducible voltammograms exhibiting a distinct reoxidation peak were obtained. The purpose of the present investigation is the study of

aluminium deposition and redissolution reactions in cryolite based melts on tungsten electrodes by using voltammetry and coulometry.

2. Experimental procedure

The melt was contained in a pyrolytic boron nitride crucible of 50 mm height and 43 mm diameter covered with a boron nitride disk to prevent excessive evaporation. Three holes were provided in the disk for the working electrode, the counter electrode and the reference electrode. The melt temperature was measured with a Pt-PtRh 10% thermocouple at the bottom of the crucible.

The cell assembly was introduced to a 600 mm long alumina tube of 70 mm diameter placed in a vertical furnace. Kanthal wire was used for resistance heating and the temperature was controlled with a Eurotherm unit. The upper and lower ends of the furnace were closed with brass covers. Fittings were provided for fixing the electrodes and for admitting inert gas. All experiments were performed under argon atmosphere; before filling with argon (99.995%) the furnace was evacuated to 10⁻² torr.

The working electrode was a 50 mm long tungsten wire (99.95%, Goodfellow Metals Ltd) of 1.15 mm diameter spotwelded to a nickel rod which was contained in an alumina sleeve. The active area which varied between 0.2 and 0.5 cm² was determined by the depth of immersion in the

*Present address: Eltech Electrosearch SA, Geneva, Switzerland.

melt (4 to 10 mm). A few experiments were performed with a 1.6 mm tungsten rod of 99% purity (Elektro-Metall AG). The counter electrode was a 1.5 mm tungsten rod immersed to a depth of 25 mm. Two types of reference electrode were used. The first type was a liquid aluminium electrode contained in a boron nitride tube with a small aperture. This electrode exhibited a potential stable to ± 10 mV, but because of attack by the liquid aluminium on the tungsten wire used as a contact, its useful life time was limited to a few hours. The second type of reference electrode consisted of a high purity nickel wire in contact with a NaF–20% NiF₂ melt contained in a hot pressed closed ended boron nitride tube acting as a diaphragm. This electrode gave satisfactory results for the present purpose.

Melts were prepared from handpicked natural Greenland cryolite (Kryolitselskabet Oresund A/S), the analysis of which yielded the following data: (The analysis was kindly performed by Analytical Laboratory of Alusuisse SA, Neuhausen). Ca < 0.01%, Si 100–1000 ppm. Cu 0.5 ppm, Ga 10 ppm, S < 0.01%, P < 0.01%, Mg, Fe, Mn, Cr below detection limit. To prepare melts of different cryolite ratios, anhydrous AlF₃ (Osark Mahoning Co., 99.7%) or analytical grade NaF (Merck, min 99%) were added to cryolite. These salts were previously dried by heating under vacuum (0.1 torr) in batches of 100 g for 2 h at 150°C, then at 300°C and finally for 1 h at 500°C.

Three experimental techniques were employed: (1) potential sweep, (2) cathodic constant current pulse followed by an anodic pulse of equal magnitude and (3) cathodic constant current pulse followed by open circuit corrosion of the electrode. The potential in the latter two techniques was monitored on an $X-t$ recorder. A potentiostat Amel Type 555) with a function-generator (Amel Type 565) and in some experiments a constant current source (Keithley Model 227) served as the power supply.

3. Results

3.1. Potential sweep experiments

A typical voltammogram obtained by starting from an open circuit in the cathodic direction with a sweep rate of 10 mV s^{-1} is shown in Fig. 1. A dis-

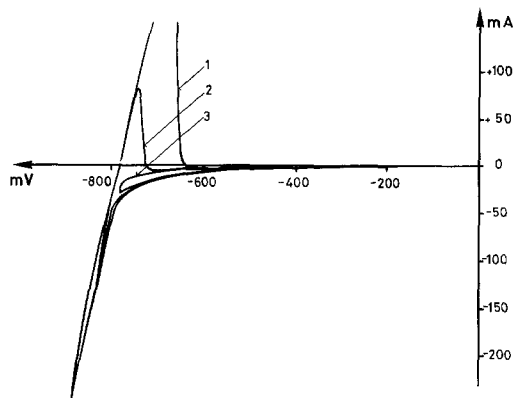


Fig. 1. Voltammograms measured in cryolite ($CR = 3$) at a sweep rate of 10 mV s^{-1} for different sweep reverse potentials: (1) -900 mV , (2) -850 mV , (3) -800 mV . Electrode area: 0.50 cm^2 , reference: Ni/Ni^{2+} .

tinct break is observed in the cathodic current trace at a potential of about 770 mV from open circuit. This break is associated with the onset of deposition at the cathode of aluminium at constant activity [6]. Upon reversing the sweep direction, the cathodically deposited metal is reoxidized, the height of the reoxidation peak being dependent on the value of the potential of sweep reversal. No reoxidation peak is observed if the sweep is reversed before the critical potential corresponding to the break in the cathodic trace has been reached. In this potential region the cathodic reaction leads to formation of dissolved species. The data of Fig. 1 were obtained in a pure cryolite melt of $CR = 3.0$ (the cryolite ratio, CR , is defined by $CR = \text{mol \% NaF/mol \% AlF}_3$). Fig. 2 illustrates that for otherwise identical conditions, the value of the current corresponding to the critical potential increases with the cryolite ratio. In pure NaF only dissolved

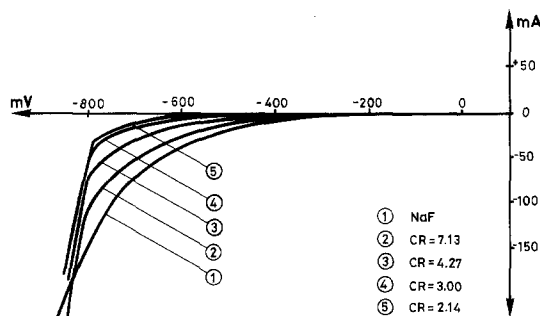


Fig. 2. Cathodic current measured at a potential sweep rate of 10 mV s^{-1} in melts of different cryolite ratios ($C \text{ mol \% NaF/mol \% AlF}_3$): Electrode area: 0.50 cm^2 , reference: Ni/Ni^{2+} .

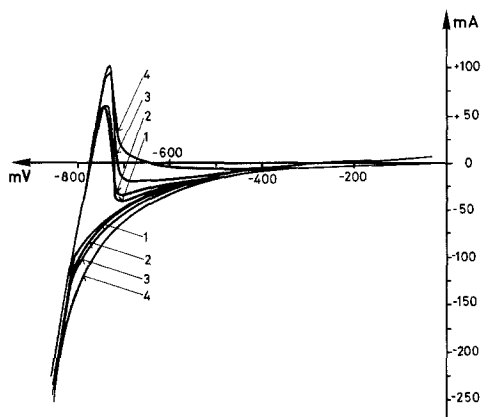


Fig. 3. Voltammograms measured at different sweep rates in a melt of $CR = 7.13$: (1) 5 mV s^{-1} , (2) 10 mV s^{-1} , (3) 20 mV s^{-1} , (4) 50 mV s^{-1} . Arrest potential: -875 mV , reference: Ni/Ni^{2+} , Electrode area: 0.50 cm^2 .

sodium is formed [6]. An increase in scan rate tends to increase the value of the current density corresponding to the critical potential as shown in Fig. 3 for a melt with a CR of 7.13. A few exploratory experiments performed with a rotating wire electrode indicated that increase in rotation speed has the same effect (Fig. 4).

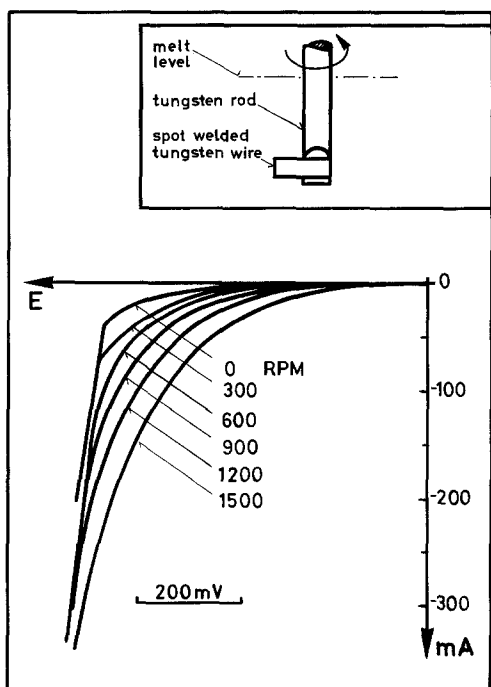


Fig. 4. Cathodic current measured with a rotating wire electrode (insert) at a sweep rate of 10 mV s^{-1} at different rotation rates. $CR = 3.0$, Electrode area: 0.49 cm^2 , reference: Ni/Ni^{2+} .

3.2 Galvanostatic pulse reversal experiments

In these experiments a cathodic constant current pulse of preset intensity and duration was applied followed immediately by an anodic pulse of equal magnitude. The resulting potential response is illustrated in Fig. 5. The data shown were obtained in pure cryolite ($CR = 3$) at current densities ranging from 20 to 180 mA cm^{-2} and a pulse length of 2 s . The observed potential response differed depending on the magnitude of the applied current: above 40 mA cm^{-2} a distinct potential arrest at about -650 mV occurred upon switching from cathodic to anodic polarity, while at lower current densities the potential immediately jumped to more positive values. The potential arrest is due to anodic oxidation of cathodically deposited aluminium. Its absence at low current densities signifies that no aluminium deposition took place under these conditions.

By multiplying the applied current density with the potential arrest time the charge density Q_a for anodic reoxidation of the deposited metal was evaluated and compared to the charge density Q_c passed during the cathodic current pulse. Results shown in Fig. 6 demonstrate that the ratio Q_a/Q_c increases with current density and is always much smaller than one. Experiments performed in melts of different cryolite ratio showed Q_a/Q_c to decrease with increasing CR .

3.3 Corrosion experiments

Constant current pulses of different intensity and length were applied and the potential decay was monitored under open circuit conditions. Fig. 7 shows measured potential transients for an applied current density of 100 mA cm^{-2} at different pulse lengths in cryolite ($CR = 3$). The length of the potential arrest after current switch off corresponds to the time necessary to spontaneously dissolve the deposited metal. As expected, the measured dissolution time increases with increasing cathodic charge. Assuming that metal loss takes place at a constant rate during cathodic deposition as well as under open circuit conditions the total time $t_c + t_d$ (t_c is the cathodic pulse time and t_d the potential decay time upon current switch off) should be a linear function of the cathodically applied charge density Q_c . Results obtained for different cathodic

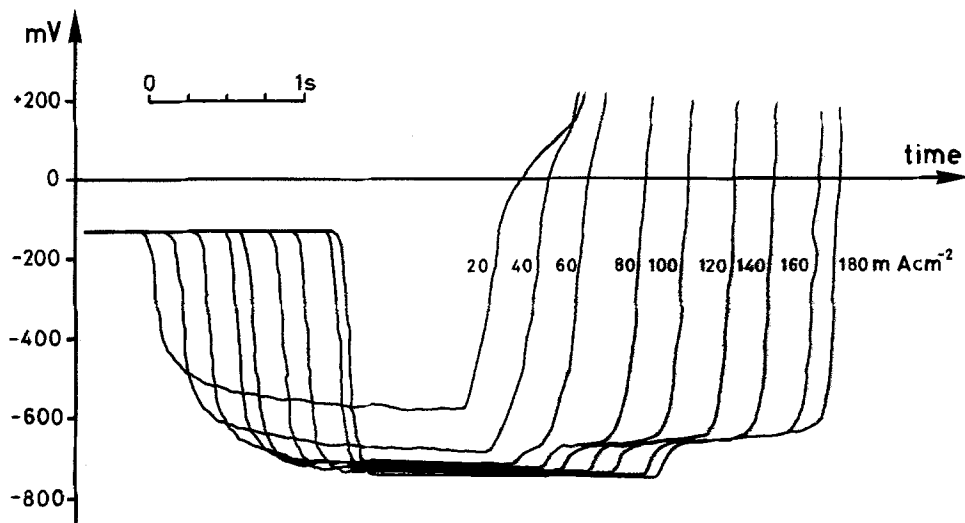
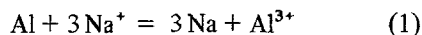


Fig. 5. Potential transients measured upon application of different cathodic current pulses followed by anodic current pulses of equal magnitude and duration. $CR = 3$, $t_c = 2s$, reference: Ni/Ni²⁺. Electrode area: 0.50 cm². The onset of the curves is shifted on the time axis for clarity of presentation.

currents comprised between 50 and 570 mA cm⁻² and deposition times comprised between 5 and 60 s shown in Fig. 8 confirm this hypothesis.

4. Discussion

It is well known that aluminium has a finite solubility in molten cryolite [1] although the exact chemical nature of the dissolved species is still unclear. Indeed, a reaction equilibrium between aluminium and sodium exists in the melt [9, 11]:



The term 'dissolved metal' will be used here to indicate the sum of dissolved aluminium and sodium. In the absence of significant activation over-

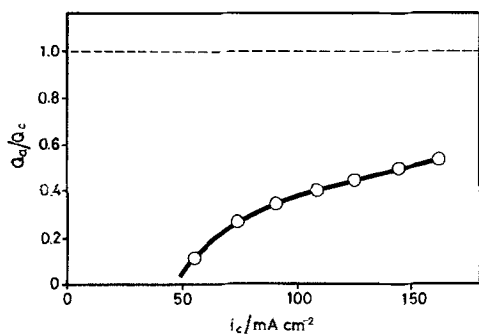


Fig. 6. Measured charge ratio Q_a/Q_c in galvanostatic pulse reversal experiments as a function of cathodic current density. $CR = 3.0$.

voltage the cathode potential is given by the Nernst Equation 2

$$E = E^0 + \frac{RT}{3F} \ln \frac{a_{Al^{3+}}}{a_{Al}} \quad (2)$$

Here a_{Al} is the activity of metallic aluminium at the surface. Two cathodic regimes can be distinguished. Above a critical potential, aluminium is actually deposited as metal or alloy at constant surface activity. Below the critical potential the reduced aluminium remains dissolved in the electrolyte, its surface activity being lower than the

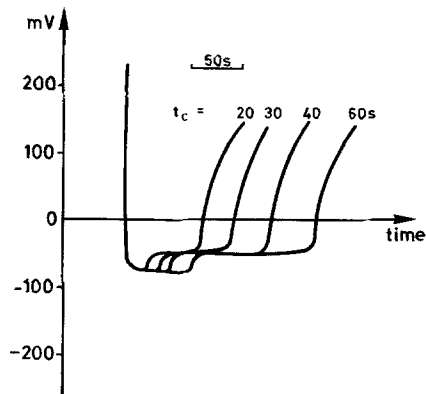


Fig. 7. Potential transients measured upon application of cathodic current pulses of different duration followed by open circuit corrosion of deposited metal. $CR = 3.0$, $i_c = 95 \text{ mA cm}^{-2}$, reference: Al/Al³⁺.

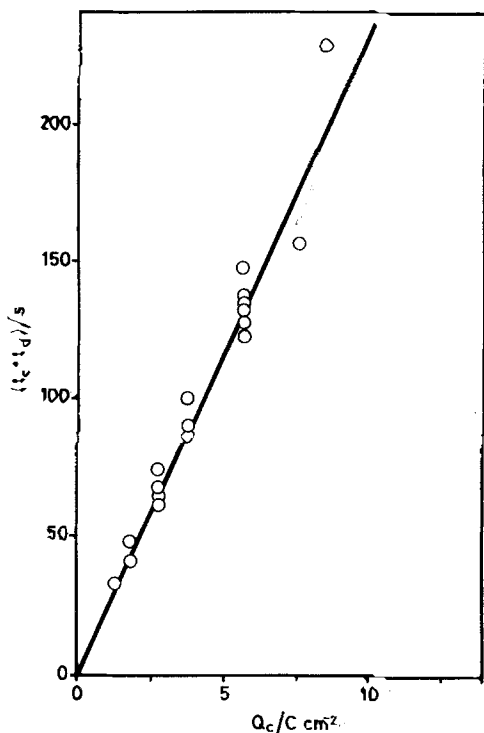


Fig. 8. Measured total time, $t_c + t_d$, as a function of cathodic charge density Q_c or galvanostatic deposition experiments followed by corrosion at open circuit, $CR = 3.0$.

fixed activity corresponding to the formation of a deposit. The finite solubility of aluminium in the melt leads to a loss of metal at the cathode which is reflected as a loss in current density, i_{loss} . It is mass-transport controlled and to a first approximation can be expressed by Equation 3:

$$i_{\text{loss}} = 3F D_M \frac{C_s}{\delta} \quad (3)$$

Here D_M is the diffusion coefficient of dissolved metal, C_s is the surface concentration of dissolved metal, δ is the Nernst diffusion layer thickness. The measured cathodic current, i_c , is the sum of the net deposition current density i_{dep} and the loss current density i_{loss} .

$$i_c = i_{\text{dep}} + i_{\text{loss}} \quad (4)$$

In the voltammetry experiments shown in Fig. 1, below the critical potential corresponding to the break in the potential trace, i_{dep} is zero and dissolved metal is produced exclusively. Under these conditions the measured current density $i_c = i_{\text{loss}}$ is governed by the rate of diffusion of dissolved

metal from the cathode into the bulk solution and its value is proportional to the concentration gradient of dissolved metal at the cathode (Equation 3). Therefore, the measured current increases with scan rate corresponding to a steeper concentration gradient at the surface. The same effect is observed while varying the rotation rate of a rotating wire electrode (Fig. 4).

Above the critical potential, aluminium is actually deposited at the surface. This is reflected by the appearance of a reoxidation peak in the reverse scan of voltammetry experiments (Fig. 1).

The current density corresponding to the critical potential for aluminium deposition increases with scan rate (Fig. 3), electrode rotation rate (Fig. 4) and with cryolite ratio (Fig. 2). The latter effect is explained by the shift of equilibrium [1] to the right. When the cryolite ratio increases the critical aluminium activity at the cathode surface is reached only at a higher total dissolved metal concentration.

In galvanostatic deposition experiments i_{loss} , to a first approximation, is independent of applied current density. As a consequence upon pulse reversal the measured ratio Q_a/Q_c should increase with increasing values of i_c . This is in agreement with the data of Fig. 6. At small current densities, $i_c \leq i_{\text{loss}}$ no metal deposition occurs i.e. the value Q_a/Q_c is zero. From Fig. 6 the limiting value of $i_c = i_{\text{loss}}$ is about 50 mA cm^{-2} .

Aluminium dissolution under open circuit conditions proceeds at a constant rate corresponding to an equivalent current density identical to i_{loss} . Its value can be estimated from the results of the open circuit corrosion experiments of Fig. 8 using Equation 5

$$i_{\text{loss}} = \frac{Q_c}{(t_c + t_d)} \quad (5)$$

The obtained value of 40 mA cm^{-2} is of the same order of magnitude as that derived from the pulse reversal experiments of Fig. 6.

Present results do not permit quantitative calculation of the rate of the cathodic loss reaction. To achieve this a closer control of mass transport conditions and a better understanding of the interactions between deposited aluminium and the substrate are required. Nevertheless the results obtained are qualitatively consistent and in agreement with the present knowledge derived from the operation of industrial aluminium cells.

Specifically, it is known that current efficiency in aluminium electrolysis is improved by lowering the cryolite ratio below 3 and/or by increasing cathodic current density [1]. According to the present data, increasing the cryolite ratio increases i_{loss} by increasing the maximum surface concentration of dissolved metal at the cathode (Equation 1). The effect of current density follows from Equation 4, which shows that in the presence of a mass transport controlled and therefore constant value of i_{loss} , an increase in current density i_c leads to a higher current efficiency for deposition, since the ratio i_{dep}/i_c increases. Thonstad and Rolseth [4] investigated aluminium deposition on a liquid cathode and found that cathodic overvoltage decreased markedly when the melt was stirred. Present results suggest that increasing the mass transport rate at the cathode has an adverse effect on current efficiency. Optimization of these two counteracting influences would require mathematical modeling of the different mass transport processes at the cathode but this is not possible at present because the relevant quantitative data are not available.

5. Conclusions

The present approach to the study of cathodic reaction phenomena in aluminium electrolysis based on the use of electrochemical transient techniques in combination with a solid substrate yields a consistent set of results. Data obtained from potential sweep, galvanostatic pulse reversal and corrosion experiments on solid tungsten in cryolitic melts point to the existence of a mass transport controlled loss reaction involving diffusion of dissolved metal from the cathode surface into the

bulk electrolyte. Further studies performed under controlled hydrodynamic conditions on different substrate materials are needed to substantiate and quantify the proposed model and to clarify the role of observed interactions between the deposit and the substrate.

Acknowledgements

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References

- [1] K. Grjotheim, C. Krohn, M. Malinovsky, K. Matiasovsky and J. Thonstad, 'Aluminium Electrolysis' Aluminium Verlag GmbH, Düsseldorf 1982.
- [2] W. E. Haupin and W. B. Frank, 'Comprehensive Treatise of Electrochemistry' Vol. 2, edited by J. O'M Bockris, B. E. Conway, E. Yeager and R. E. White, Plenum Press (1981) p. 301.
- [3] K. Grjotheim, C. Kohn, R. Naenmann and K. Torklep, *Metall. Trans.* **1** (1970) 3133.
- [4] J. Thonstad and S. Rolseth, *Electrochim. Acta* **23** (1978) 223.
- [5] J. J. Del Campo, J. P. Millet and M. Rolin, *ibid.* **26** (1980) 59.
- [6] J. J. Duruz, G. Stehle and D. Landolt, *ibid.* **26** (1981) 771.
- [7] M. Hansen, K. Anderko, 'Constitution of Binary Alloys' 2nd edition, McGraw Hill, London and New York, (1958) p. 147.
- [8] K. A. Bowman, PhD thesis, University of Tennessee (1977).
- [9] S. Wilkening and H. Ginsberg, *Metall.* **27** (1973) 787.
- [10] K. Yoshida and E. W. Dewing, *Metall. Trans.* **3** (1972/73) 1817.
- [11] J. C. Mitchell and C. S. Samis, *Trans. Metall. Soc. AIME* **245** (1969) 1227.
- [12] R. S. Nicholson and I. Shain, *Anal. Chem.* **36** (1964) 706.