PERFORMANCE OF ALUMINUM DEPOSITION FROM CHLORIDE MELTS

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ABSTRACT

Aluminum deposition from KCl/AlCl₃, NaCl/AlCl₃, and LiCl/AlCl₃ melts at variable temperatures (but at 700°C in most experiments) involves several factors which are detrimental for obtaining high current yields:

(i) Chlorine is dissolved in the melts and decreases current efficiencies for Al deposition by reoxidation of dispersed aluminum and by direct chlorine reduction at the cathode. Increasing chlorine solubilities and hence decreased current efficiencies are observed with increasing AlCl₃ concentration in the melt and --at least in melts of low AlCl₃ content-- with increasing temperature (1).

(ii) Dispersion (and subsequent reoxidation of dispersed aluminum) is favored at cathodes which are poorly wetted by Al, especially at vertical cathode faces in front of which the electrolyte is stirred vigorously by evolved chlorine gas. Carbon, due to the formation of thin Al carbide coatings, is not the most suitable cathode material because it is poorly wetted by liquid Al.

(iii) Higher oxygen content (Al₂O₃) in melts results in CO at the carbon anode which gives rise to rapid anode deterioration and -- since CO readily dissolves as COCl₂ in the melts -- in enhanced reoxidation of aluminum (yielding additional contamination of the electrolyte by finely dispersed carbon particles). For these reasons it seems desirable to change the technique for Al deposition from chloride melts by introducing well-wetted cathodes and dimensionally stable (i.e. non-corroding) anodes. The introduction of suitable diaphragms may also be of some advantage.

INTRODUCTION

Since the publication of ALCOA's patents (2), interest in the technique of aluminum electrowinning from chloride melts has increased steadily.

It is well-known that the ALCOA method still has to cope with some difficulties among which is a lower current...
yield than for Al deposition in the Hall-Heroult electrolysis.

Only very little is known about the details of the ALCOA process. Therefore, some experiments on Al deposition from NaCl-AlCl₃ melts were performed in a cell which allowed the visual observation of the electrolysis in order to obtain additional information on fluid dynamics and general physical behavior of electrolyte, gases and deposited metal within the electrolysis cell.

EXPERIMENTAL PROCEDURE

Fig. 1 depicts schematically the apparatus used which was constructed with the aim to allow visual inspection of the process, especially the dispersion of electrodeposited metal (forming either brown fog or small but distinguishable droplets), the fluid dynamic behavior of the melt in front of the anode and the cathode, and formation of carbon particles and other insoluble materials in the melt.

The electrolysis vessel consisted of a quartz tube (quartz is relatively stable in chloride melts and is etched only very slowly by release of some SiCl₄ or SiO₂, respectively, into the melt). The vessel was heated by a gas burner and was insulated thermally by an asbestos screen equipped with an asbestos window which could be removed intermittently for visual inspection of the electrolysis process.

The electrodes (as indicated in Fig. 1) could be arranged vertically and horizontally at any desired distance between 5 mm and 50 mm. The aluminum electrode, immersed in the same electrolyte as used for electrolysis, was taken as reference electrode (R. Al el.). The reference electrode was connected to the measuring electrode by the usual (quartz) Luggin capillary. In some cases a diaphragm made of hard sintered Al₂O₃ (Staatliche Porzellanmanufaktur Berlin) was put between the vertically arranged electrodes. The electrolyte was prepared from thoroughly dried alkali chlorides. AlCl₃ was purified initially by double sublimation and later by distillation at pressures under 2 bars. Fig. 2 shows the vapor pressure of aluminum chloride vs temperature in order to demonstrate that AlCl₃ can be refluxed easily in the laboratory by applying conventional means and apparatus.

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RESULTS

a) Voltammetry of Al deposition was performed on solid and liquid aluminum surfaces and at carbon electrodes. The voltammetric curves for Al deposition from LiAlCl$_4$, NaAlCl$_4$ and KAlCl$_4$ melts were very similar. Fig. 3a shows the voltammogram measured for deposition and dissolution of aluminum at liquid aluminum surface from a melt containing 60 mole % KCl and 40 mole % AlCl$_3$. The current-voltage curve shows some hysteresis (10 to 15 mV) but in general it exhibits (up to a current density of 100 mA/cm$^2$) nearly ohmic behavior with a formal impedance of 0.8 $\Omega$ cm$^2$ which must be due to an uncorrected IR-drop in the electrolyte (because of experimental reasons the tip of the Luggin capillary could only be kept at a minimal distance of 1 cm from the surface; $\kappa$(KAlCl$_4$) = $10^{-7}$ cm$^{-1}$). Thus Al deposition and dissolution seem to proceed completely reversibly (as expected).

Fig. 3b shows the voltammogram measured at a carbon electrode (Sigri BK 02). The voltage range extends from -200 mV up to + 2.5 V vs rev. Al el. so that the process of Al deposition as well as of Cl$_2$ evolution is observed.

Whereas chlorine evolution does not exhibit any peculiarities, the prewave of cathodic Al deposition is remarkably different from Al deposition on Al surfaces and very typical for Al deposition at carbon cathodes. The completely irreversible anodic peak with a current maximum at 1 V is due to reversal of the cathodic process observed by appearance of the prewave. The half-peak potential (+ 300 mV) of the cathodic prewave which is not mass transfer controlled and instead is attributed to a process which consumes current ($\int_1^t$ dt) proportional to the area of the electrode, leads to the assumption that the cathodic prewave is due to aluminum carbide formation ($\Delta^{o}$ (Al$_4$C$_3$) = 385.870 kJ/mol corresponding to a calculated formation potential of + 0.33 V vs rev. Al el.).

Since aluminum carbide is an insulator, it covers and blocks the carbon surface very effectively so that on further cathodic polarization and further increase of cathodic current, aluminum deposition and formation of liquid aluminum droplets may be observed only at singular points of the carbon surface. The mean surface density of active sites where aluminum is actively deposited as droplets does not exceed several ten to twenty per cm$^2$. 

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b) Preparative Al deposition from NaCl/AlCl₃ (45/55 mole %) Melts. The aim of these experiments was to investigate the influence of electrode geometry (horizontal/vertical) and electrode wettability (by liquid aluminum) on current yields of cathodic Al deposition.

For these experiments the following electrode arrangements were used:

a) Two rectangular vertical electrodes (2 x 4 cm²) with an electrode gap of 5 mm (upper electrode pair in Fig. 1)

b) Two circular electrodes horizontally arranged with an electrode gap of 5 mm (lower electrode pair in Fig. 1). The upper circular electrode was a perforated plate with approx. 50% transparency and 2 mm Ø of the holes and served as chlorine evolving anode.

All experiments were performed with anodes made of graphitized carbon (Sigri BK 02) but different cathode materials were chosen. Total current-voltage curves were measured over the current density range 0.01 to 1.5 A/cm² and by extrapolation to zero current density "experimental decomposition potentials" were obtained.

Fig. 4 shows in its lower part the temperature dependence of the theoretical decomposition potential of NaCl-AlCl₃ melts (45 mole % AlCl₃, 55 mole % NaCl) in comparison to the "experimental decomposition potentials" of these melts and the measured cell voltages at standard current densities of 0.5 A/cm². Experimental decomposition potentials as well as experimentally determined cell voltages are influenced only slightly by the choice of the respective cathode materials (less than 50 mV at the highest current density of 1.5 A/cm²). This observation clearly shows that under stationary conditions Al deposition proceeds always at fresh Al surfaces. The upper part of Fig. 4 shows schematically what occurs at the carbon anode and cathode, respectively, at current densities of 0.5 A/cm² in the temperature range from 200° to 750°C.

Cathode behavior. At the cathode finely dispersed dendritic deposits are observed as long as the working temperature lies below the Al melting point of 660°C. In no case was it possible to melt down this metal powder to liquid metal because, due to traces of moisture or oxygen present in the melt, the small aluminum crystals are covered by a layer of alumina which prevents coagulation of the metal powder on melting. Below 660°C current...
efficiencies for cathodic Al deposition are therefore always assumed to be virtually zero (Table 1). The situation is quite different for Al deposition above 660 °C. Then on carbon electrodes many small aluminum droplets are formed which on horizontally arranged cathodes eventually coalesce to form larger droplets or even a closed aluminum surface or pool which covers the cathode surface completely. On vertical carbon electrodes, however, the Al droplets which do not wet the surface show only very little tendency to coalesce. Instead it is observed very often that smaller aluminum droplets literally "explode" into the melt where a brown and glittering cloud of finely dispersed and minute aluminum droplets is formed which slowly settles to the bottom of the electrolyzer vessel. Usually the melt in an undivided cell is strongly agitated by anodically generated chlorine so that parts of this metal mist are moved to the anode where they undergo, at least partially, reoxidation to aluminum chloride. Furthermore, homogeneously dissolved chlorine (I) consumes some dispersed aluminum metal so that due to this pronounced and undesired metal dispersion at carbon electrodes, current yields for cathodic aluminum and anodic chlorine production do not exceed 50% (second row, Table 1). At a horizontal carbon cathode lying below a perforated anode, current yields improve dramatically (to near 90%) provided the carbon cathode is covered completely by a "pool" of molten aluminum, so that the aluminum deposits on a completely closed surface of molten aluminum (row 4, Table 1). As long as small single droplets can be distinguished at the cathode, the "explosion" phenomena continue to occur and give rise to dispersion even at horizontal carbon cathodes; current efficiency does not exceed 60%. It should be stressed that the use of a perforated horizontal anode above the horizontal cathode reduces greatly the convective motion of the electrolyte because the chlorine gas is allowed to escape through the electrode holes.

If instead of carbon cathodes, iron, steel or other cathode materials (TiB₂) are used which are "wetted" by liquid aluminum (i.e. at which the wetting angle of liquid aluminum approaches zero), then even at vertically arranged cathodes liquid aluminum is deposited with current efficiencies very close to 100%. There is a distinct influence of the nature of the electrolyte on current efficiencies of Al deposition on carbon anodes. Cathodic current efficiencies obtained at vertical carbon cathodes decrease from ~45% to below 20% if KCl/AlCl₃ (60/40) is used instead of NaCl/AlCl₃ (60/40). This seems to be due to the enhanced chlorine solubility in
KAICl₄ melts compared to NaAlCl₄ melts (compare in (1) the difference between LiAlCl₄ and CsAlCl₄ melts).

Anode behavior

The pronounced chemical instability of the anode at lower temperature is most important, which is very likely due to the formation of chlorine-aluminum chloride-graphite intercalation compounds (4). These intercalation compounds are formed preferentially at the graphite grain boundaries so that the matrix of the graphitized carbon is destroyed rapidly. Because the Cl₂ decomposition pressure of the intercalation compound increases with increasing temperature, graphite anodes become more stable at higher temperatures. They are stable for no longer than ~10 minutes at 250°C. Around 500°C their stability is somewhat better but only above 620°C they may be assumed to be reasonably stable. Nevertheless there is some doubt that graphite may be really a perfectly dimensionally stable anode because it may be corroded at high temperature by formation of carbon tetrachloride. According to JANAF- tables the equilibrium constant for CCl₄ formation at 700°C amounts to

$$K_p (CCl_4) \text{ at } 1000 K = 7 \cdot 10^{-3} \text{ bar}^{-1}$$

so that in the presence of 1 bar of chlorine an equilibrium partial pressure for CCl₄ of nearly 10⁻² bars has to be taken into account. The equilibrium constant for CCl₄ formation decreases with increasing temperature, so that carbon anodes become more stable at higher temperatures.

c) Cathodic Al deposition in the presence of Al₂O₃

Some electrolysis experiments were performed upon the addition of 2.5 to 3.5 mole % Al₂O₃. The presence of oxo-anions in the melts at such high concentrations is very disadvantageous for the performance of cathodic Al deposition at any cathode material, whereas at carbon anodes the oxo-anions are preferentially discharged to form CO or COCl₂ which is dissolved in the melt. At the cathode in the presence of Al₂O₃ one observes that

(i) Droplets of liquid aluminum which do not stay in contact with the cathode react relatively rapidly with dissolved phosgene to form Al oxychloride and carbon.
4 Al + 3 COCl₂ + 3 AlOCl + 3 C + AlCl₃  (2)

Single aluminum droplets are soon covered with a thin carbon layer and redissolve (depending on their size) in 10 to 20 minutes.

(ii) Because aluminum oxochloro complexes are discharged at the electrode preferentially (5), the oxo-ion concentration at the cathode increases to an extent which exceeds the solubility product of Al₂O₃. Aluminum oxide is coprecipitated with aluminum (and carbon) so that no longer a smooth cover of Al (on well wetted cathodes) or a multitude of single Al droplets (on non-wetted carbon electrodes) is deposited but a firmly adhering sludge of Al/Al₂O₃/C from which aluminum cannot be recovered and which, after some time, blocks the cathode or fills the electrode gap giving rise to anode/cathode short circuits. In KAlCl₄ melts these reactions decrease current efficiency to a larger extent than in NaAlCl₄ melts because CO, COCl₂ and Al₂O₃ solubilities seem to be higher in K-melts than in Na- (or Li-) melts.

Cathodic Al deposition at vertical electrodes of different cathode materials

Since poor Al wettability of carbon cathodes gives rise to dispersion and reoxidation of aluminum, different metals were investigated as cathode materials in order to evaluate their suitability. All of these metals are wetted well by liquid Al.

Table 2 compares the results for Al deposition obtained in short-term experiments (3 to 8 hrs) with current densities of 0.5 A/cm² in KCl/AlCl₃ (60/40) melts for carbon and the wettable metals stainless steel, titanium, zirconium, tungsten, and the refractory material TiB₂ (from Elektroschmelzwerk Kempten GmbH). At all wettable metal cathodes comparable current efficiencies were obtained. As expected, stainless steel is strongly attacked by dissolution into the liquid aluminum (which is nearly saturated with iron). Titanium and zirconium cannot be used either since they are rapidly alloyed and further deteriorate by dissolution of the base metal into liquid aluminum (which was not expected from the published phase diagrams). Tungsten is stable for a short time, but a thorough inspection reveals that after only 8 hours of operation, there is some deterioration due to the
beginning of alloying with aluminum. Only titanium diboride does not show any deterioration.

Thus it is quite clear that refractory metal compounds like carbides and borides with free enthalpy of formation which exceeds the free enthalpy of Al alloying may be used as wettable cathodes. Ti, Zr and W (and particularly steel) may be used only as support materials for those refractory metals if a perfectly dense layer of the refractory material can be formed on the metal support.

CONCLUSION

The aim to develop further aluminum electrowinning from chloride melts by decreasing cell voltages below 3.5 V (for instance by reducing still further the electrode distance) and by raising simultaneously current efficiencies might call for a new cell concept which uses separator divided cells with vertical electrodes. For this purpose, but with some benefit from ALCOA's technology, solutions for the following material problems should be found in:

1) Development of low-cost cathodes which are wetted by aluminum but have a low solubility in it (refractory metals or materials coated by refractory metals).

2) Development of non-carbonaceous anodes with high intrinsic electrical conductivity, anodic corrosion resistance and low Cl₂ overvoltage.

3) Development of corrosion resistant and electrically insulating materials for cell bodies, tubes, and heat exchangers, which would allow to handle the anodically generated chlorine at temperatures up to 1000 K.

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### Table 1

**Deposition Yields for Cathodic Al Deposition**

| Electrode                          | Temperature (°C) | Al current yield          |
|-----------------------------------|-----------------|---------------------------|
| graphite horizontal and vertical  | 200 - 650       | virtually 0               |
| graphite vertical                  | 600             | small droplets 40 - 50 %  |
| graphite horizontal                | 660             | larger droplets 45 - 60 % |
| Al-regulus horizontal              | 660             | 95 %                      |
| iron or other wetting cathodes     | 660             | 95 %                      |

### Table 2

**Performance of Different Cathode Materials For Al Deposition (From KCl/AlCl₃:60/40 Melts)**

| Cathode Material       | Current Yield [%]* | Material Performance                          |
|------------------------|---------------------|-----------------------------------------------|
| Carbon (EK 78, Sigri)  | 15                  | Stays intact                                  |
| Stainless steel        | 63                  | Surface corrosion by dissolution              |
| Titanium               | 68                  | Deteriorated by alloy formation and dissolution |
| Zirconium              | 78                  | Deteriorated by alloy formation and dissolution |
| Tungsten               | 60                  | Slightly changed by alloy formation           |
| TiB₂**                 | 85                  | Material unchanged                           |

* Mean value of several experiments performed from 3 to 8 hours each.
** Delivered from Elektroschmelzwerk Kempten.
Fig. 1

Fig. 2
Fig. 3a

Fig. 3b

Electrolyte: NaAlCl₃ + 0.1AlCl₃

Fig. 4