ABSTRACT

The cathodic deposition of aluminium from chloride melts has been studied at 975K (702°C) on tungsten and glassy carbon electrodes. The melts studied were dilute solutions of AlCl₃ (5x10⁻⁵ - 3.5x10⁻⁴ mol cm⁻³) in binary equimolar mixtures of LiCl-NaCl, NaCl-KCl and NaCl-CsCl. Measurements were performed using electrochemical relaxation methods.

In the LiCl-NaCl and the NaCl-KCl systems, the reduction reaction seems to be rather fast and contributions from diffusion are mainly observed. On tungsten electrodes the response exhibits effects of alloying. The diffusion coefficient for the diffusing species calculated from results on glassy carbon electrodes, was about 4.5x10⁻⁵ cm²s⁻¹ in the LiCl-NaCl system and about 2.6x10⁻⁵ cm²s⁻¹ in the NaCl-KCl system.

In the NaCl-CsCl system a slow nucleation process is observed. The differences in the rate of phase formation in the three systems are discussed based on variations in the interfacial tension of the melt electrode interface.
INTRODUCTION

Several studies of aluminium deposition on different substrates in chloride melts have been reported. Schulze and Hoff /1/ and Rolland and Mamantov /2/ studied the deposition of aluminium from acidic chloro-aluminate melts at low temperatures. Sal'nikov et al. /3/ and Gol'dshein et al. /4/ studied the deposition of aluminium from NaCl-KCl-AlCl₃ melts on tantalum electrodes and liquid aluminium electrodes at 700-800°C. Ødegård et al. /5/ studied the same system also including tungsten electrodes and the binary NaCl-AlCl₃ melt. Gabco et al. /6/ used glassy carbon and tungsten electrodes in binaries of AlCl₃ with NaCl, KCl and CsCl. Some differences in the interpretation of the results from measurements in basic melts are found. The main dispute concerns whether the reaction is purely diffusion controlled or whether a mixed control involving a charge transfer reaction /5/ or a preceding dissociation of a complex is present /6/. In acidic melts, Takahashi and Komura /7/ found intermediates in the reduction of complex Al(III) species in the melt and interpreted this as a monovalent ionic aluminium species.

EXPERIMENTAL

Experiments were carried out in a gold film furnace (Trans Temp Inc., USA). The experimental cell was a transparent quartz tube. As working electrodes (WE) glassy carbon (GC) rods, 3mm Ø, type GC-30 from Tokai Carbon Co., Ltd., Japan and tungsten (W) rods, 2 or 4 mm Ø (99.9% purity) from the Tungsten Manufacturing Co.Ltd., England, were employed. After being mirror polished, both types of electrodes were encapsulated in boron nitride with the lower circular cross section exposed to the melt. The apparent area was 0.071 cm² for the glassy carbon electrodes and 0.035 cm² or 0.125 cm² for the tungsten electrodes. Super-purity aluminium (99.999%) contained in a corundum tube in contact with the bulk melt served as reference electrode (RE). In all cases the base electrolyte was an equimolar binary mixture of alkali chlorides. Aluminium chloride (Fluka, iron-free) was purified by distillation in vacuum. Sodium chloride and potassium chloride (Merck, extra pure) were purified by heating under vacuum, melting and recrystallization in argon atmosphere. Lithium chloride and caesium chloride were heated in
HCl atmosphere, at 400°C and then filtrated in vacuum.

The aluminium chloride content was determined by atomic absorption spectrophotometry from melt samples. The temperature was kept constant at 975 ± 1K for all runs. Argon gas flowing through the cell was purified by magnesium perchlorate to remove moisture and by titanium sponge at 600°C to remove oxygen. The cathodic reaction was studied by use of linear sweep voltammetry, chronoamperometry and chronopotentiometry. Measurements were carried out with a PAR Model 173 potentiostat/galvanostat with an IR compensation unit and a PAR model 175 Universal programmer. Slow responses were measured by an X-Y recorder whereas fast responses were recorded and stored on a Nicolet Explorer III A oscilloscope.

RESULTS AND DISCUSSION

The glassy carbon electrode

The LiCl:NaCl-AlCl₃ and NaCl:KCl·AlCl₃ systems

Cyclic voltammograms for the deposition of aluminium from NaCl-KCl-AlCl₃ melts on glassy carbon electrodes are shown in Fig. 1. On the glassy carbon electrode the reduction starts immediately when the potential reaches the reversible value for the aluminium electrode. A sharp cathodic peak corresponding to a very narrow anodic peak and with IP much higher then IC, indicate the deposition and stripping of an insoluble product. The amount of charge during the cathodic half cycle equals that during the anodic half cycle. At low sweep rates (up to 200 mV s⁻¹) the IP vs. v¹/₂ plots (Fig. 2) exhibits straight lines which, within the experimental error, pass through the origin. Additionally, the peak potential remains constant at -25 mV, which is almost exactly the same as the theoretical value of -24mV for a diffusion controlled deposition of an insoluble product with the discharge of three elementary charges. Both features show the diffusion controlled nature of aluminium deposition at low cds. Similar results were also obtained from voltammetric measurements in the LiCl-NaCl-AlCl₃ melt.

Results from chronoamperometric measurements in the NaCl-KCl-AlCl₃ system are shown in Fig. 3 as limiting current values from potentiostatic transient plotted
vs. $t^{-1/2}$. The results show excellent agreement with the Cottrell equation confirming the diffusion controlled nature of the reaction.

In Fig. 4 galvanostatically obtained transition times are plotted as $\tau_{0.5}$ vs $i^{-1}$ from measurements in the LiCl-NaCl-AlCl$_3$ system (curve 1 and 3 for the GC electrode). No sign of a preceding dissociation reaction is observed.

The NaCl-CsCl-AlCl$_3$ system

Voltammograms obtained in the NaCl-CsCl-AlCl$_3$ melt on GC electrodes seem not to be very different from the corresponding diagrams in the two other melts. When plotting the results in a $I_p$ vs $v^{1/2}$ diagram, the difference is obvious as shown in Fig. 5. The curves do not pass through the origin, a feature which points to nucleation control. Current time transients for this system from potentiostatic measurements on a GC electrode are shown in Fig. 6. For comparison one transient from the LiCl-NaCl system is also plotted in the figure. The transients exhibit features of a nucleation process but are not typical either of instantaneous or progressive nucleation. The multiple maxima at higher potentials and times show similarities to transients corresponding to repeated nucleation of several mono-layers of metal /8/.

One singular current-time transient on a GC electrode is shown in Fig. 7 as a plot of $I_q$ vs $t^{-0.5}$. The reaction is obviously not controlled purely by diffusion. The same is shown in Fig. 8 which exhibits results from chronopotentiometric measurements also on GC electrodes. The two transients in Fig. 8 show both an overshoot of the initial deposition potential of 60-70 mV. The straight lines in the $t^{0.5/i^{-1}}$ plot in Fig. 9 do not intersect the origin. All these facts are pointing to a nucleation process that plays a part in the overall control of the reaction. Also in the two systems with LiCl-NaCl and NaCl-KCl melts initial potential overshoots in the voltammetric and the chronopotentiometric measurements were observed, but only in a few cases, and always on fresh electrode surfaces (during the first deposit). These overshoots were insignificant, however, only about 5 mV in magnitude.
The tungsten electrode

Voltammograms for the tungsten electrode are shown in Figs. 10 and 11. A common feature for all the melt systems using this electrode is the cathodic depolarization due to alloy formation between aluminium and tungsten. Aluminium starts to deposit at potentials positive to the reversible potential. This leads to a broadening of the wave and a reduction of the peak cd. The anodic wave is rather different in the three systems. In the NaCl-KCl system, a single anodic wave is observed, a wave which is broadened compared with the anodic wave on GC electrodes. This broadening increases with sweep rate. In the LiCl-NaCl (Figs. 10 and 11) and the NaCl-CsCl systems two more or less distinct anodic waves, denoted by symbols b and e in Fig. 10, are observed. In the LiCl-NaCl system, wave e appears before wave b when the cathodic potential limit is moved to more negative values during cyclic sweeping. In Fig. 11, it is observed that $I_{p}/I_{s}$ decreases with the number of sweeps during repeated cyclic sweeping before reaching a stable value. It seems that wave b in such cases is reduced from a distinct peak to a shoulder. In all the systems the anodic charge is less than the cathodic charge. All these facts show that aluminium is alloyed with tungsten. From the phase diagram of the Al-W system /9/ it is known that a liquid alloy containing 1-2 wt% W is found at 700°C on the aluminium rich side. This phase is in equilibrium with a solid peritectic $\delta$ phase and further a high melting peritectic $\epsilon$ phase with somewhat higher tungsten content. Peak b then probably corresponds to the oxidation of aluminium from the liquid alloy whereas peak e corresponds to the oxidation of aluminium in the peritectic compound. That this is a compound is likely from the very steep descent of the anodic branch, showing that the aluminium activity is rather constant during the oxidation. That the $I_{p}/I_{s}$ ratio decreases during repeated scans can be explained as a result of an accumulation of aluminium in the tungsten lattice forming more of the above mentioned compound and that the rate of diffusion of aluminium in the lattice increases with repeated cycling. It is known that the concentration of vacancies increases in the surface layer during the so-called development of an alloy electrode /10/.
The prepeak

On the tungsten electrode, a cathodic prepeak at about +0.35 V was found, corresponding to a nearly symmetrical reversed peak only slightly moved in the anodic direction. Signs of these peaks are observed in all the systems, but are especially clear in the LiCl-NaCl system as shown in Fig. 10 and expanded in Fig. 12, with the corresponding peaks denoted by d for the cathodic and c for the anodic peak. The peak potential is nearly independent of sweep rate, at sweep rates up to 500 V s\(^{-1}\). The ratio of the cathodic peak current to the peak current of the main peak (peak a) increases with sweep rate and is larger than unity at a sweep rate of 500 V s\(^{-1}\). At high sweep rates the peak current seems to be directly proportional to the sweep rate. It was also observed that the anodic charge is slightly greater than the cathodic charge which means that aluminium is still retained in the tungsten after the main anodic peaks b and e.

The nature of the prewave is not clear. It has the features of an adsorption wave because of its reversibility and the linearity of the peak current with sweep rate. On the other hand however, the coulombic charge involved corresponds to about 100 monolayers of aluminium. It seems that some sort of a surface compound is formed, a compound which is retained through the main deposition-stripping cycle. One possibility is the formation of a monovalent Al species at the surface by a partial charge transfer. Such a species would probably be more stable in the LiCl-NaCl system where the activity of AlCl\(_3\) is much higher than in the two other systems.

The diffusion coefficient

The diffusion coefficient has been calculated from the results of all three methods for both electrodes in all the three melt systems. The results are shown in Table 1. In case the deposition reaction is not purely diffusion controlled, the diffusion coefficient is an apparent one.

For the GC electrode in the LiCl-NaCl-AlCl\(_3\) and the NaCl-KCl-AlCl\(_3\) systems the results are very consistent, with values of about 4.5x10\(^{-5}\) cm\(^2\) s\(^{-1}\) in the former system and about 2.6x10\(^{-5}\) cm\(^2\) s\(^{-1}\) in the latter system.
For the tungsten electrode in the same systems, the values differ considerably. The values determined by the chronopotentiometric and the chronoamperometric methods are of the same level as for the GC electrode. The voltammetric values, however, are considerably lower. This is easily explained by the alloying of the deposit with the substrate which leads to a broadening of the cathodic wave and therefore to a reduction of the peak current. The diffusion coefficient is calculated by use of the equation for an insoluble deposit, an equation which is not strictly correct for this type of behaviour. The equation for an ideally soluble product (a redox system) should not be correct either.

Table 1 Diffusion coefficients determined by different methods in three melts on tungsten and glassy carbon electrodes.

| Method       | Li-Na-Al | K-Na-Al | Cs-Na-Al |
|--------------|----------|---------|----------|
| I GC         | 4.6±0.4  | 2.5±0.4 | 1.8±0.5  |
| W            | 3.0±0.5  | 1.5±0.6 | 1.2±0.3  |
| II GC        | 4.6±0.4  | 2.5±0.2 | 4.2±0.8  |
| W            | 4.4±0.4  |         | 3.2±0.5  |
| III GC       | 4.4±0.3  | 2.7±0.3 | 0.4      |
| W            | 4.6±0.2  | 2.8±0.2 |          |

I - Voltammetry
II - Chronopotentiometry
III - Chronoamperometry

For the NaCl-CsCl-AlCl₃ system, the results differ extensively between the three measuring methods. The results from the chronopotentiometric method compare well with the two other systems whereas the potential controlled methods and especially the potentiostatic (chronoamperometric) method results in much lower values. This confirms the nucleation control in this system which leads to a low value of the current in the current-time transient before nucleation is taking part. The apparent diffusion coefficient is then too low. In the galvanostatic method, however, a constant rate is imposed on the interface setting up a corresponding diffusion gradient which leads to a more
"correct" value of the transition time and the calculated diffusion coefficient.

The rate of the charge transfer reaction

The rate constant for the rate controlling step of the heterogeneous charge transfer reaction was determined by potential sweep voltammetry at high sweep rates in the LiCl-NaCl and the NaCl-KCl systems. The $E_p$ vs log $v$ diagram for one series in the NaCl-KCl system is shown in Fig.13. The peak voltage is constant up to about 0.1 Vs$^{-1}$ and increases then with log $v$ at higher rates. The relation becomes rather linear at rates higher than about 100 Vs$^{-1}$. The linearity in this plot indicates that the IR-compensation has been rather effective. From such plots a rate constant of about 0.2 cm s$^{-1}$ was found in both melts.

THE MECHANISM OF THE REACTION

At the low concentrations used in these investigations the aluminium deposition reaction is mainly diffusion controlled in the stationary case. In the LiCl-NaCl and the NaCl-KCl systems the phase formation seems to be rather fast whereas clear evidence of a nucleation control was found in the NaCl-CsCl system, on glassy carbon electrodes but also on tungsten electrodes even if in this case there is an alloy formation. The reason for this is not obvious but has to be connected with the interfacial properties of the system. The most likely explanation is based on differences in interfacial energy. The lighter alkali chlorides, LiCl and NaCl have very high surface tensions 116.2 dyn cm$^{-1}$ for LiCl and 116.1 dyn cm$^{-1}$ for NaCl at 900°C /11/. The surface tension of KCl is 97.0 dyn cm$^{-1}$ and for CsCl as low as 79.5 dyn cm$^{-1}$ at 800°C. This means that the NaCl-CsCl melt wets the electrode surface far better than especially the LiCl-NaCl melt. In the LiCl-NaCl melt, the new molten Al phase is then easily formed and spreads on the electrode interface, perhaps as an extremely thin metal film due to the inferior wetting of the melt. In the CsCl-NaCl system, small nuclei are probably formed in the shape of miniature droplets with a contact angle depending on the surface forces. The apparent repeating feature of the process is difficult to explain. The maximum point does
probably not correspond to the formation of a completely covered surface.

No signs of a preceding chemical reaction, which most likely would be the dissociation of a complex, were found even in the CsCl containing system. An increase in the product \( i^{1/2} \) from galvanostatic measurements at low \( \text{cds} \) is probably due to the role of convection in the mass transfer at times longer than a few seconds. By moving the electrode at these conditions, an immediate effect of convection on the current was observed. This probably means that the deposition takes place directly from the prevailing AlCl\(_4\) complex ion in these melts or that the complex dissociates quickly before the charge transfer.

The slowest step in the electrodic reaction in the LiCl-NaCl and the NaCl-KCl melt could either be the charge transfer reaction itself or the phase formation. The \( (\partial E_p/\partial \log v) \) value of 160-200 mV corresponds to a theoretical value of about \( RT/F \). This points to a rate controlling step comprising two elementary charges which could not be the phase formation step. In the CsCl-NaCl system, however, phase formation is the rate controlling electrodic step.

REFERENCES

1. K. Schulze and H. Hoff, Electrochim. Acta 17 (1972) 119.
2. P. Rolland and G. Mamantov, J. Electrochem. Soc. 123, (1976) 1299.
3. V.I. Sal'nikov, V.P. Butorov, B.V. Mel'nikov, V.A. Lebedev and I.P. Nichkov, Soviet Electrochem. 10, (1974) 1142.
4. S.L. Gol'dshtein, Z.P. Raspopin and V.A. Fedorov, Soviet Electrochem. 13, (1977) 1545.
5. R.Ødegård, A. Bjørgum, A. Sterten, J. Thonstad and R. Tunoid, Electrochim. Acta 21, (1982) 1595.
6. M. Gabco, P. Fellner and Z. Lubyova, Electrochim. Acta 22, (1984) 397.
7. S. Takahashi and N. Koura, Denki Kagaku 50, (1982).
8. J. A. Harrison and H. R. Thirsk in Electroanalytical Chemistry ed. A. J. Bard, Vol 5 (1971) 67.
9. M. Hansen, Constitution of binary alloys, McGraw-Hill Book Company, New York (1958).
10. Z. Astakhov, Yu. Filinovsky and G. Teplitskaya, Electrokhimiya 13, (1977) 566.
11. B. Berge and J. L. Holm, Rapport til NTH's Fond 14.11.1970 Institute of Inorganic Chemistry, The Technical University of Norway, Trondheim.
Fig. 1. Cyclic voltammograms.
Sweep rate (mV s⁻¹): 1:10; 2:20; 3:50; 4:75; 5:100.
Glassy carbon WE; \(c_{\text{AlCl}_3} = 4.72 \times 10^{-4} \text{ mol cm}^{-3}\),
Electrode area: 0.071 cm², NaCl-KCl equimolar melt.

Fig. 2.
The cathodic peak current vs. square root of sweep rate in NaCl-KCl equimolar melt.
1: tungsten WE; \(c_{\text{AlCl}_3} = 4.20 \times 10^{-4} \text{ mol cm}^{-3}\)
2: tungsten WE; \(c_{\text{AlCl}_3} = 4.95 \times 10^{-4} \text{ mol cm}^{-3}\)
3: glassy carbon WE; \(c_{\text{AlCl}_3} = 4.07 \times 10^{-4} \text{ mol cm}^{-3}\)
4: glassy carbon WE; \(c_{\text{AlCl}_3} = 4.68 \times 10^{-4} \text{ mol cm}^{-3}\)
electrode areas; tungsten: 0.035 cm², glassy carbon: 0.071 cm².
Fig. 3.
Diffusion limiting current vs. \( t^{-1/2} \) from potential step measurements in NaCl-KCl equimolar melt.
1: glassy carbon WE; 
\[ c_{\text{AlCl}_3} = 5.47 \times 10^{-4} \text{ mol cm}^{-3} \]
2: tungsten WE; 
\[ c_{\text{AlCl}_3} = 5.47 \times 10^{-4} \text{ mol cm}^{-3} \]
3: glassy carbon WE; 
\[ c_{\text{AlCl}_3} = 3.59 \times 10^{-4} \text{ mol cm}^{-3} \]
electrode area GC: 0.071 cm\(^2\)
4: tungsten WE; 
\[ c_{\text{AlCl}_3} = 4.39 \times 10^{-4} \text{ mol cm}^{-3} \]
electrode area W: 0.035 cm\(^2\).

Fig. 4. Variations of \( \tau^{1/2} \) with \( i^{-1} \) from chronopotentiometric measurements in NaCl-KCl equimolar melt. Glassy carbon WE; 
\[ c_{\text{AlCl}_3} = 3.53 \times 10^{-4} \text{ mol cm}^{-3} \].
Fig. 5.

The cathodic peak current vs. square root of sweep rate in NaCl-CsCl equimolar melts.
1: $c_{\text{AlCl}_3} = 3.21 \times 10^{-4} \text{ mol/cm}^3$
2: $c_{\text{AlCl}_3} = 2.01 \times 10^{-4} \text{ mol/cm}^3$
3: $c_{\text{AlCl}_3} = 0.91 \times 10^{-4} \text{ mol/cm}^3$
4: $c_{\text{AlCl}_3} = 0.52 \times 10^{-4} \text{ mol/cm}^3$
GC working electrode.

Fig. 6. Current versus time from potential step measurements in NaCl-CsCl equimolar melt.
$c_{\text{AlCl}_3} = 2.13 \times 10^{-4} \text{ mol/cm}^3$

The dotted line is taken from a similar experiment in LiCl-NaCl equimolar melt. The curve is corrected for a small difference in the concentration of AlCl$_3$. Glassy Carbon working electrode.
Fig. 7. Diffusion limiting current vs $t^{-1/2}$ from potential step measurements in NaCl-CsCl equimolar melts. Glassy carbon working electrode. $c_{AlCl_3} = 6.14 \times 10^{-5}$ mol/cm$^3$.

Fig. 8. Chronopotentiometric measurements in NaCl-CsCl equimolar melt. Glassy carbon working electrode $c_{AlCl_3} = 8.67 \times 10^{-5}$ mol/cm$^3$. $i_1 = 0.4$ Acm$^{-2}$; $i_2 = 0.5$ Acm$^{-2}$
Fig. 9. Variations of $i r^{1/2}$ with $i^{-1}$ from chronopotentiometric measurements in NaCl-CsCl equimolar melts. Glassy carbon working electrode.
1: $c_{\text{AlCl}_3} = 1.25 \times 10^{-4}$ mol/cm$^3$
2: $c_{\text{AlCl}_3} = 2.20 \times 10^{-4}$ mol/cm$^2$
3: $c_{\text{AlCl}_3} = 0.87 \times 10^{-4}$ mol/cm$^3$.

Fig. 10. Cyclic voltammogram in LiCl-NaCl equimolar melt.
W Electrode, $v = 20$ mVs$^{-1}$
$c_{\text{AlCl}_3} = 2.08 \times 10^{-4}$ mol cm$^{-3}$
Fig. 11. Repetitive cyclic voltammograms at a tungsten electrode in LiCl-NaCl equimolar melt, $v = 50 \text{ mV s}^{-1}$, $c_{\text{AlCl}_3} = 1.09 \times 10^{-4} \text{ mol cm}^{-3}$.

Fig. 12. Cyclic voltammograms of prewaves d and c in equimolar LiCl-NaCl melt at different sweep rates (mV s$^{-1}$): 1:200; 2:300; 3:500; 4:1000. $c_{\text{AlCl}_3} = 1.97 \times 10^{-4} \text{ mol cm}^{-3}$.
Fig. 13. Cathodic peak potential vs. log v, from voltammetric measurements in NaCl-KCl equimolar melt. Glassy carbon WE, $c_{\text{AlCl}_3} = 5.84 \times 10^{-5}$ mol cm$^{-3}$. 