

Aluminium electrodeposition from AlCl_3 -NaCl melts on glassy carbon, platinum and gold electrodes

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The electrochemical deposition and dissolution of aluminium on glassy carbon, platinum and gold electrodes in chloraluminates melts have been investigated using linear sweep voltammetry and potentiostatic pulse techniques. It was shown that deposition of aluminium on the glassy carbon electrode at low overpotentials takes place by 3-D progressive nucleation and growth, with the incorporation of atoms in the crystal lattice as the rate-determining step. At overpotentials higher than -100 mV vs Al, in the melts containing more than 52 mol % of AlCl_3 , diffusion of Al_2Cl_7^- takes over the control of deposition of aluminium. Alloying of platinum and gold electrodes with aluminium from the melt occurs in the underpotential region.

1. Introduction

The processes of electrochemical deposition and dissolution of aluminium in AlCl_3 -NaCl melts have been studied mainly on aluminium electrodes [1-5], except for the reduction of Al_2Cl_7^- ions, which was investigated at glassy carbon, platinum and tungsten electrodes [6]. Recently, glassy carbon was used for investigation of the deposition of aluminium from AlCl_3 -NaCl melts [7-10] and for the first time a rotating ring-disc electrode was used for this purpose [11].

It was shown that aluminium could be deposited from the melt as a pure metal, but there are some ambiguities concerning the kinetics and mechanism of deposition [1, 6-10]. The latest investigations pointed out that 3-D nucleation is involved in the deposition process [6-10].

In this connection the results of an investigation of aluminium electrodeposition on glassy carbon, platinum and gold electrodes from AlCl_3 -NaCl melts of different compositions are presented.

2. Experimental details

All experiments were carried out in an electrochemical cell designed for work in melts, under a purified nitrogen atmosphere. The cell was made of Pyrex glass and placed in a furnace.

Discs of glassy carbon (Atomergic Company) and platinum (99.999%) and a gold wire (99.999%) were used as working electrodes, while the counter electrode was a glassy carbon rod, all sealed in Pyrex tubes. High-purity aluminium rod (m5N, 99.999%,

Alfa Products, Thiokol/Ventron Division) was used as the reference electrode.

The working electrodes were first mechanically polished on emery papers grade 0, 00, 000 and 0000 and then on polishing cloths (Buehler Ltd) impregnated with Al_2O_3 (Banner Scientific Ltd), $1\ \mu\text{m}$, $0.3\ \mu\text{m}$ and $0.05\ \mu\text{m}$, grades. The reference electrode was cleaned in solutions of 50 vol % HF + 15 vol % H_2O_2 and conc. NH_4OH + 5 vol % H_2O_2 , prior to each experiment. All glassware, including working, reference and counter electrodes, was washed with triply distilled water and alcohol and dried in a vacuum at 120°C for at least 1 h before use.

Sodium chloride, p.a. (Merck), was dried in a furnace at 500°C for 6 h and kept in vacuum at 120°C until use. Aluminium(III) chloride [puriss, > 99% Cl; Fe < 0.008% (Fluka AG)], was not dried before using.

The procedure of melting the AlCl_3 -NaCl mixture consisted of heating (in an inert atmosphere) a vessel with AlCl_3 at the bottom and NaCl on top at 250°C , until all the AlCl_3 sublimated and made an AlCl_3 -NaCl melt by reaction with NaCl.

After melting, the mixture was pre-electrolysed between two aluminium plates (99.999%) of large surface area ($20\ \text{cm}^2$ each) for 10 h, with constant current density of $1.5\ \text{mA cm}^{-2}$ at 220 - 250°C . Both aluminium plates were cleaned before use, in the same way as the reference electrode.

Linear sweep voltammetry and potentiostatic pulse techniques were applied by using a Universal programmer (PAR-M175), a potentiostat (PAR-M173) and an X-Y-t recorder (Houston Instrument 2000R).

The temperature of the melt was controlled by using

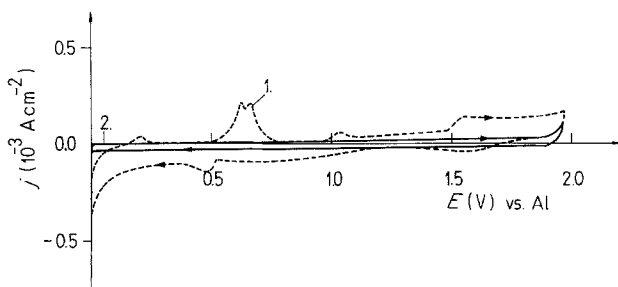


Fig. 1. Linear sweep voltammograms of the glassy carbon electrode obtained in an equimolar melt at 200°C with a sweep rate of 10 mV s^{-1} : (1) without pre-electrolysis; (2) after 10 h of pre-electrolysis with $j = 1.5 \text{ mA cm}^{-2}$ at 220–250°C.

a thermocouple (Chromel–Alumel, Omega Engineering Inc.) with an accuracy of $\pm 1^\circ \text{C}$.

3. Results

The linear sweep voltammograms of the glassy carbon electrode obtained in the non-purified (1) and purified (2) melts, in the potential region positive to the potential of the aluminium reference electrode, are shown in Fig. 1. It is seen that after 10 h of pre-electrolysis, all impurities are removed from the melt (voltammogram 2).

The potentiostatic j - t transients of aluminium deposition on the glassy carbon electrode, obtained in the melt before pre-electrolysis (1) and after pre-electrolysis (2) are shown in Fig. 2. It is seen that the presence of impurities significantly changes the shape of the j - t transients.

The presented results were obtained in an equimolar melt (50.0 mol % AlCl_3 –50.0 mol % NaCl), but the influence of impurities was almost the same in all the investigated compositions of the melt.

Further results are related to the pre-electrolysed melts.

3.1. Melt of equimolar composition

The linear sweep voltammograms with well-defined

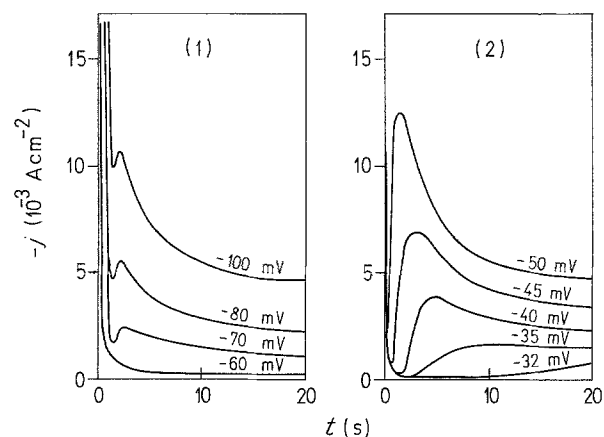


Fig. 2. Potentiostatic j - t transients of aluminium deposition on the glassy carbon electrode obtained in an equimolar melt at different overpotentials (marked in the figure) and at 200°C: (1) without pre-electrolysis; (2) after 10 h of pre-electrolysis with $j = 1.5 \text{ mA cm}^{-2}$ at 220–250°C.

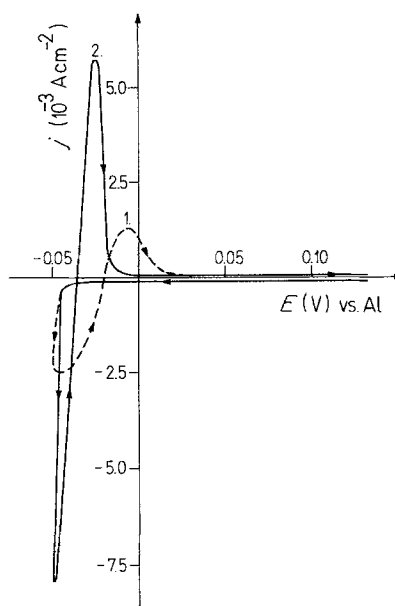


Fig. 3. Linear sweep voltammograms of aluminium deposition and dissolution on the glassy carbon electrode, obtained at two different temperatures of the melt, are shown in Fig. 3. It is seen that cathodic and anodic currents increase with increasing temperature of the melt. The cross-over potential between the cathodic and anodic current is seen not to coincide with the reference electrode potential.

‘crystallization loops’ of aluminium deposition and dissolution on the glassy carbon electrode, obtained at two different temperatures of the melt, are shown in Fig. 3. It is seen that cathodic and anodic currents increase with increasing temperature of the melt. The cross-over potential between the cathodic and anodic current is seen not to coincide with the reference electrode potential.

If the substrates are platinum and gold, the linear sweep voltammograms are different, indicating that some interaction between these two substrates and depositing aluminium occurs at potentials positive to the reference potential of aluminium (Figs 4 and 5). The amount of aluminium deposited in the under-potential region increases with holding the working platinum and gold electrodes at a potential of 0.0 V vs Al, as can be seen in Fig. 6 for the platinum electrode.

The potentiostatic j - t transients of aluminium

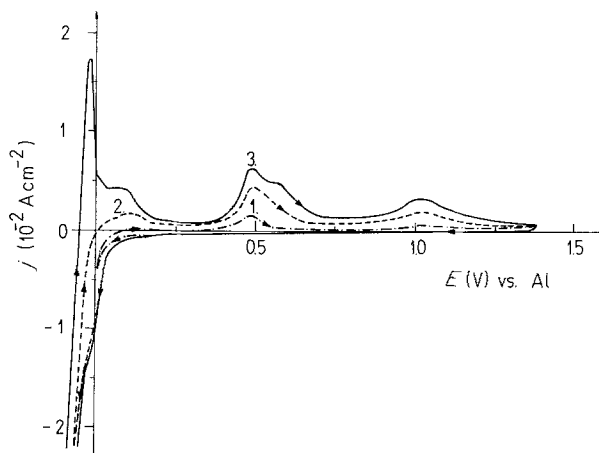


Fig. 4. Linear sweep voltammograms of aluminium deposition and dissolution on the platinum electrode obtained in equimolar melt at 250°C with a sweep rate of 50 mV s^{-1} . Cathodic limiting potentials: (1) 0; (2) -60; (3) -100 mV vs Al.

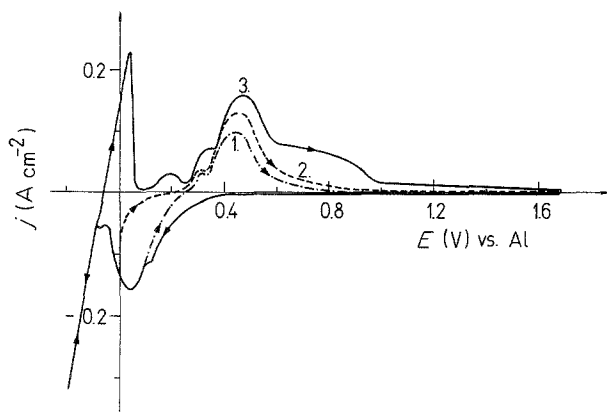


Fig. 5. Linear sweep voltammograms of aluminium deposition and dissolution on the gold electrode obtained in equimolar melt at 250°C with a sweep rate of 50 mV s^{-1} . Cathodic limiting potentials: (1) 100; (2) 0; (3) -200 mV vs Al .

deposition on glassy carbon, platinum and gold electrodes are shown in Fig. 7, indicating that aluminium could also be deposited on platinum and gold electrodes in the underpotential region.

3.2. Melts with more than 50 mol % of AlCl_3

If the amount of aluminium(III) chloride in the melt exceeds 50.0 mol %, a further wave appears on the voltammogram of deposition and dissolution, as seen in Fig. 8 for a melt composition of 52 mol % AlCl_3 -48 mol % NaCl . The same shapes of voltammogram are obtained in melts containing 55 mol % of AlCl_3 and 60 mol % of AlCl_3 , indicating that the process of aluminium deposition takes place by two electrochemical reactions at two different potentials.

The linear sweep voltammograms of aluminium deposition and dissolution on the glassy carbon electrode, obtained in melts containing 50 and 60 mol % of AlCl_3 are compared in Fig. 9, showing that they are almost identical in the region negative to the potential of aluminium in the equimolar melt, Al_{st} .

The potentiostatic j - t transients on the glassy carbon electrode from melts containing more than 50.0 mol % of AlCl_3 are almost the same in all investigated melts (melts with 52, 55 and 60 mol % of AlCl_3). They are shown in Fig. 10 for the melt composition 55 mol % AlCl_3 -45 mol % NaCl . It is seen that the

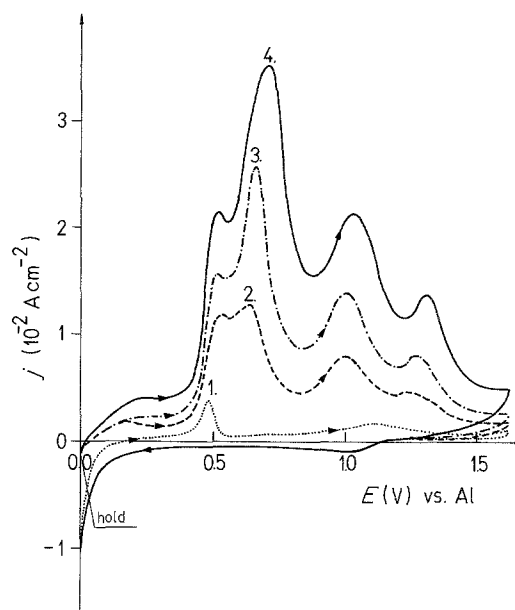


Fig. 6. Linear sweep voltammograms of aluminium dissolution from the platinum electrode obtained in an equimolar melt at 200°C with a sweep rate of 50 mV s^{-1} , after holding the working electrode at a potential of 0.0 V vs Al for: (1) 0; (2) 60; (3) 120; (4) 180 s.

shape of the transients depends on the applied overpotential and that at overpotentials higher than -400 mV vs Al the depositing current suddenly rises, indicating that a new electrochemical reaction commences.

The rising portions of the j - t transients, obtained at low overpotentials, on the glassy carbon electrode from the melt containing 55 mol % of AlCl_3 are shown in Fig. 11. They are almost the same in all investigated compositions of the melt, including the equimolar melt. The result of the analysis of the j - t transients presented in Fig. 11 is shown in Fig. 12, indicating that aluminium deposition on the glassy carbon electrode takes place by the mechanism of 3-D progressive nucleation and growth.

At potentials more negative than -100 mV vs Al in melts containing more than 50.0 mol % AlCl_3 (Fig. 10), the shape of the j - t transients indicates that the electrochemical process is diffusion controlled. This is indeed proved by the linearity of the j - $t^{-1/2}$ dependencies obtained, shown in Fig. 13.

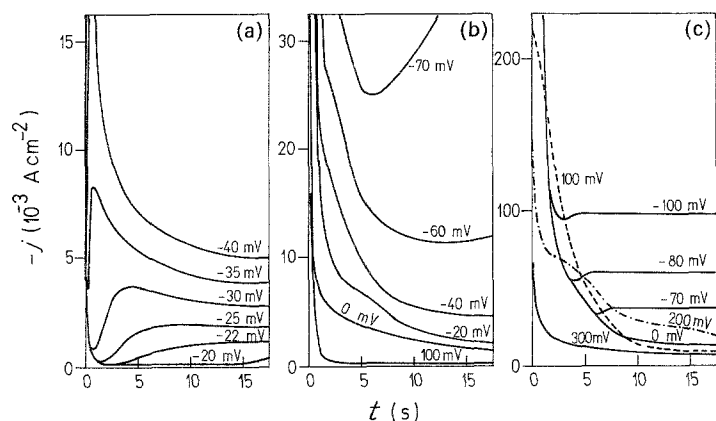


Fig. 7. Potentiostatic j - t transients of aluminium deposition on different electrodes at different overpotentials (marked in the figure) obtained in an equimolar melt at 250°C . (a) Glassy carbon; (b) platinum; (c) gold.

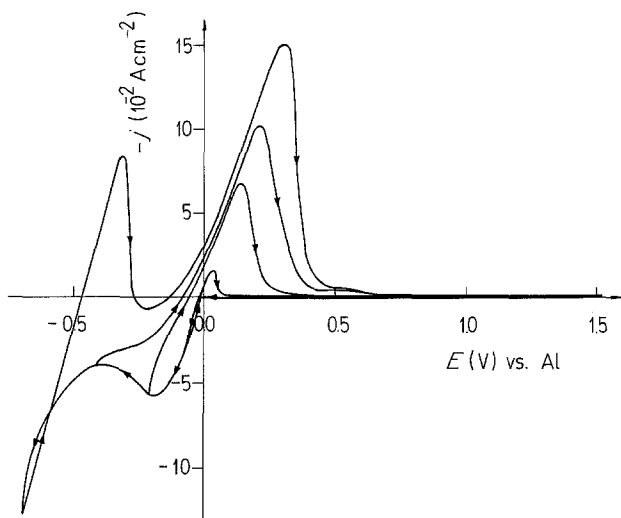


Fig. 8. Linear sweep voltammograms of aluminium deposition and dissolution on the glassy carbon electrode obtained in the melt of composition 52 mol% AlCl_3 -48 mol% NaCl at 200°C with a sweep rate of 50 mV s^{-1} .

4. Discussion

4.1. Influence of impurities

The small amount of iron present in the aluminium(III) chloride can significantly influence the process of aluminium deposition from AlCl_3 - NaCl melt. Cathodic and anodic peaks at potentials of about 0.5 V vs Al , present on the voltammogram obtained in the melt which was not purified by pre-electrolysis (curve 1 of Fig. 1), may be ascribed to the deposition of iron from Fe^{2+} and dissolution of

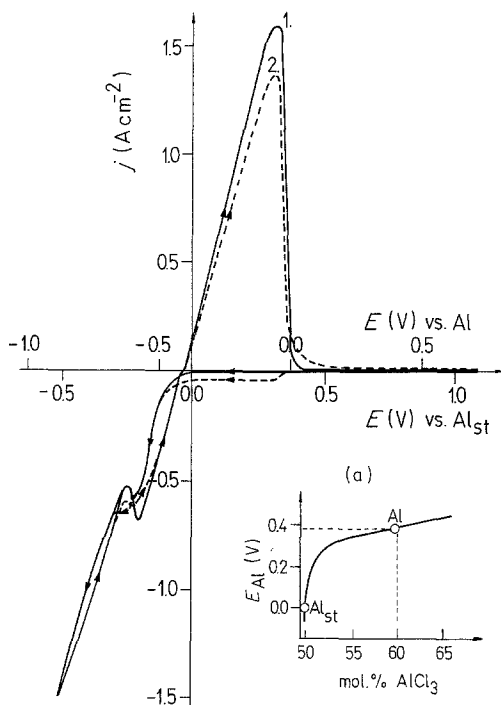


Fig. 9. Linear sweep voltammograms of aluminium deposition and dissolution on the glassy carbon electrode obtained in the melt of different compositions at 200°C with a sweep rate of 50 mV s^{-1} : (1) 50 mol% AlCl_3 -50 mol% NaCl ; (2) 60 mol% AlCl_3 -40 mol% NaCl . (a) The change of the potential of aluminium reference electrode with composition of the melt (diagram from the literature [15, 16]).

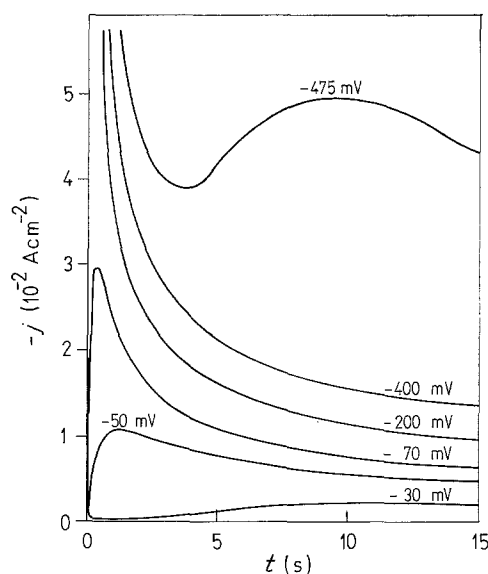


Fig. 10. Potentiostatic j - t transients of aluminium deposition on the glassy carbon electrode at different overpotentials (marked in the figure) in the melt of composition 55 mol% AlCl_3 -45 mol% NaCl at 200°C .

deposited iron, while a small peak at potential of about 1.5 V vs Al may be the result of the electrochemical reaction $\text{Fe}^{3+} + e = \text{Fe}^{2+}$ [12]. These peaks become more pronounced if the concentration of iron in the aluminium(III) chloride is higher, as is the case for technical grade chemicals [7]. After 10 h of pre-electrolysis, all iron is removed from the melt and a typical 'double layer charging' voltammogram is obtained in the potential region from 0.0 to 1.9 V vs Al . How the presence of impurities influences the aluminium deposition process is seen in Fig. 2. The process of 3-D nucleation and growth (the rising portions of the j - t transients) is completely masked because of the codeposition of impurities.

4.2. Deposition of aluminium on the glassy carbon electrode

It is known from the literature [13-18] that AlCl_3 - NaCl melts contain several different species (AlCl_3 ,

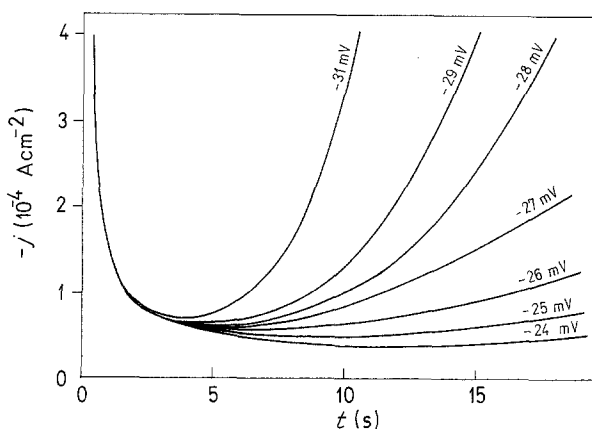


Fig. 11. The rising portion of the potentiostatic j - t transients of aluminium deposition on the glassy carbon electrode obtained at low overpotentials in the melt of composition of 55 mol% AlCl_3 -45 mol% NaCl at 250°C .

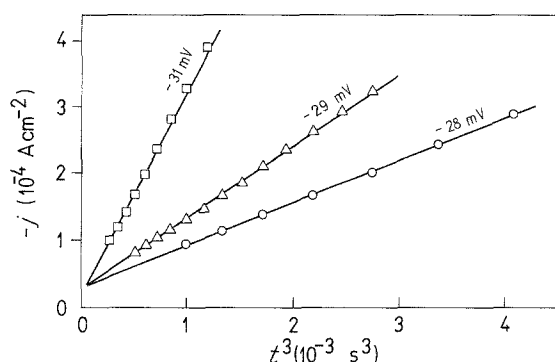


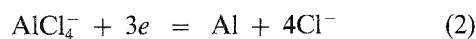
Fig. 12. The $j-t^3$ dependencies obtained by analysis of the current/time transients presented in Fig. 11.

Al_2Cl_6 , AlCl_4^- , Al_2Cl_7^- , $\text{Al}_3\text{Cl}_{10}^-$, Na^+ and Cl^-) and that the concentration of these species depends on the composition of the melt [15, 16]. In the melt with composition of 50.0 mol % AlCl_3 -50.0 mol % NaCl (NaAlCl_4), only AlCl_4^- and Na^+ species are present, while at higher contents of AlCl_3 , the concentration of Al_2Cl_7^- increases and at about 60 mol % AlCl_3 the concentrations of AlCl_4^- and Al_2Cl_7^- in the melt are almost identical [15, 16]. Accordingly, the reference potential (the potential of aluminium metal in the melt) also changes, as shown in Fig. 9a.

The two waves on the voltammograms in the melts containing more than 50 mol % of AlCl_3 (Figs 8 and 9) may be ascribed to deposition (and dissolution) of aluminium from two different species present in the melt [6, 8-10]. The first wave corresponds to reduction of Al_2Cl_7^- by the reaction



while in the second wave two reactions occur, reaction 1 and reduction of AlCl_4^-



If the concentration of Al_2Cl_7^- in the melt is negligible, as is the case in an equimolar melt, only reaction 2 occurs.

As is seen in Figs 8 and 9, two dissolution peaks exist on the voltammogram only if the amount of deposited aluminium by the second reaction 2 is small, so that it may be completely dissolved during the reverse sweep, before the electrode potential reaches the value of the 'reversible' potential of the first reaction 1. If the cathodic limiting potential is very negative and the amount of deposited aluminium by reaction 2 is very high, only one dissolution peak exists on the voltammogram, as seen in Fig. 9 (curve 2).

Using the potential of the aluminium reference electrode in the equimolar melt (NaAlCl_4) as the 'standard potential' (Al_{st}), it is possible to compare linear sweep voltammograms obtained in melts with 50 mol % of AlCl_3 and 60 mol % of AlCl_3 (voltammograms 1 and 2 of Fig. 9). It is seen that voltammograms of aluminium deposition from AlCl_4^- (potential region negative to Al_{st}) are almost the same in both investigated melts, showing that aluminium deposition from Al_2Cl_7^- has little influence on the total process of deposition. According to the shape of voltammogram

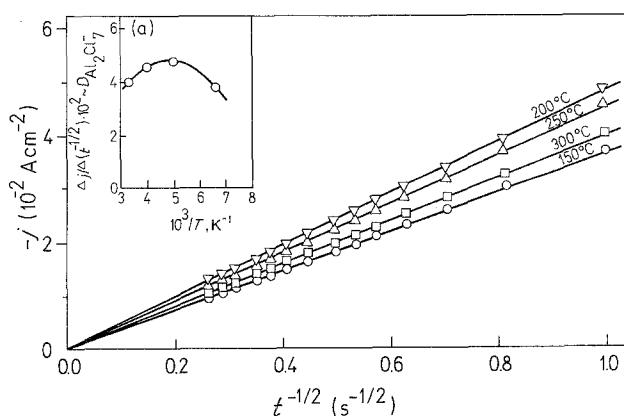


Fig. 13. The $j-t^{-1/2}$ dependencies obtained by analysis of the current/time transients of aluminium deposition on the glassy carbon electrode at overpotential of -200 mV vs Al in the melt of composition of 55 mol % AlCl_3 -45 mol % NaCl at different temperatures (marked in the figure). (a) The change of the slope of $j-t^{-1/2}$ dependencies with inverse temperature of the melt.

2, aluminium deposition from Al_2Cl_7^- should be diffusion controlled and may provoke dendritic growth of aluminium. Such an effect was not observed, and even the deposits obtained at high current densities (over -0.6 A cm^{-2}) were relatively smooth, without visible dendrites.

Potentiostatic $j-t$ transients of aluminium deposition from the melt containing more than 50 mol % AlCl_3 (Fig. 10) are in good agreement with the results of linear sweep voltammetry, showing that at overpotentials higher than -400 mV vs Al, e.g. ~ -20 mV vs Al_{st} , the new process commences and the cathodic current suddenly rises, provoking a change of the shape of the $j-t$ transients ($j-t$ transient obtained at -475 mV vs Al).

The shape of the $j-t$ transients obtained at low overpotentials (up to -70 mV vs Al) in all investigated compositions of the melt (Figs 7 and 11), indicates that aluminium deposition on the glassy carbon electrode takes place by 3-D nucleation and growth. The linear $j-t^3$ dependencies shown in Fig. 12, obtained by analysis of $j-t$ transients of Fig. 11, indicate that aluminium deposition takes place by progressive 3-D nucleation and growth with the rate-determining step being the incorporation of atoms into the growing 3-D centers [19]. The mechanism of deposition at low overpotentials is the same for all investigated compositions of the melt (including equimolar melt), showing that the type of species that must be reduced does not influence the mechanism of aluminium deposition on the glassy carbon electrode. At higher melt temperatures, for the same overpotential, the mechanism of deposition does not change but the rate of 3-D nucleation and growth becomes faster.

In the melts with more than 50 mol % AlCl_3 , incorporation of atoms into the crystal lattice is the rate-determining step only at low overpotentials (up to -100 mV vs Al), while at higher overpotentials the $j-t$ transients fall monotonically, indicating that diffusion of Al_2Cl_7^- takes over the control of the deposition process. The linear $j-t^{-1/2}$ dependencies shown in Fig. 13, obtained by analysis of the $j-t$ transients of

deposition at overpotentials of -200 mV vs Al, are in line with this conclusion [20]. The same dependencies could be obtained at all overpotentials between -100 and -400 mV vs Al.

It is interesting to note that a change of the slope of the $j-t^{-1/2}$ dependencies with inverse temperature of the melt is not linear. Knowing that the slope of the $j-t^{-1/2}$ dependence is proportional to the diffusion coefficient and the concentration of depositing species [20], the anomalous change in the diffusion coefficient with temperature (shown in Fig. 13a) partly reflects the changes in the composition and the structure of the melt with increasing melt temperature.

4.3. Deposition of aluminium on platinum and gold electrodes

Linear sweep voltammograms of aluminium deposition (and dissolution) on the platinum (Fig. 4) and gold electrodes (Fig. 5) and the potentiostatic $j-t$ transients of aluminium deposition on these two electrodes (Fig. 7), clearly show that some interaction between the substrates and the aluminium from the melt occurs at potentials positive to the potential of the aluminium reference electrode (the 'reversible potential' of aluminium). It is seen on the voltammograms that the charge under the anodic peaks reflecting the underpotential deposition, depends on the value of the cathodic potential limit, indicating that alloying between substrates and aluminium occurs. If the working electrode is held at the potential of the reference electrode (and also at potentials positive to that value up to about 200 mV), the amount of dissolved aluminium increases, as shown in Fig. 6. The shape of the anodic part of the voltammogram changes and after holding the platinum electrode at a potential of 0.0 V vs Al for 3 min (voltammogram 4), five dissolution peaks appear on the voltammogram. Knowing that platinum and gold [21] make several intermetallic compounds with aluminium, these peaks could be ascribed to the dissolution of aluminium from different intermetallic compounds [22–24]. Alloying of platinum and gold with aluminium in the underpotential region becomes more pronounced with increasing melt temperature, indicating that diffusion of aluminium in the solid state becomes faster at higher temperatures.

Acknowledgements

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