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Electrodeposition of titanium from chloride melts

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The kinetics of the electrodeposition and electrocrystallisation of titanium were studied in alkali chloride melts. Voltammograms showed two distinct anodic peaks for the oxidation steps Ti/Ti (II) and Ti(II)/Ti(III) at 70 mV and 300 mV, respectively, referred to titanium. The cathodic reduction Ti(III)/Ti(II) was very irreversible, showing an extended cathodic wave and a shoulder on the Ti(II)/Ti reduction peak. The Ti(II)/Ti reduction was found to be quasi reversible. The rate constant at 450° C was $\sim 5 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$. The diffusion coefficient in KCl–LiCl eutectic was $\sim 1 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at 450° C rising to $3.5 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ at 650° C. Potential step measurements gave curves indicating slow instantaneous nucleation and growth (I against $t^{1/2}$) followed by slow diffusion control (I against $t^{-1/2}$). During constant current steady state deposition the nature of the deposit depended on the composition of the melt, the temperature and the cd. In KCl–LiCl melts coherent deposits were obtained for cds of 60–120 mA cm^2 while higher current densities gave dendritic and spongy deposits.

1. Introduction

Commercial production of titanium metal is based on metallothermic reduction of $TiCl_4$. However, titanium can also be produced by electrolysis. It is more than 80 years since deposition of titanium by fused salt electrolysis was reported for the first time by Huppertz [1], who claimed to have obtained a reasonably pure product by electrolysis of TiO_2 dissolved in $CaCl_2$. At present, $TiCl_4$ seems to be the most suitable raw material for electrowinning of titanium. A stepwise reduction to the intermediate stages $TiCl_3$ and $TiCl_2$ is expected before titanium metal is deposited at the cathode. This process could be performed in either alkali chloride or alkali fluoride/chloride based systems at temperatures from 450 to 850° C. In chloride melts the temperature can be lowered substantially (to 120° C) by addition of $AlCl_3$ [2]. Over the previous 30 years extensive studies have been conducted with the aim of developing an electrolytic process for the reduction of $TiCl_4$ in molten salts. At present such a process is about to be commercialized [3].

The cathodic reduction of titanium from its highest oxidation state is believed to proceed by three successive electron transfer steps:

$$\mathrm{Ti(IV)} + e^- \longrightarrow \mathrm{Ti(III)} \qquad (1)$$

$$\mathrm{Ti(III)} + e^- \longrightarrow \mathrm{Ti(II)} \qquad (2)$$

$$\mathrm{Ti(II)} + 2e^- \longrightarrow \mathrm{Ti(0)} \qquad (3)$$

Electrochemical studies of titanium deposition have been carried out in various molten salt systems; chlorides, fluorides and mixtures of chlorides and fluorides. The presence of fluorides leads to stabilization of Ti(III), and the deposition of titanium may occur directly from a trivalent species. In fluoride/chloride mixtures, Ti(III) is thought to be reduced directly to the metal [4]. In pure fluoride melts (FLINAK) the TiF_6^{2-} species was found to be reduced to titanium metal from Ti(III) [5]. Chassaing *et al.* [6] showed that Ti(III) is also stable in molten CsCl at 700° C. However, the metal deposition took place via Ti(II). When the temperature was lowered to 400° C, the reduction to titanium was found to take place in one step from Ti(III). At a titanium anode dissolution occurs by the reverse reaction

$$\mathrm{Ti(0)} \longrightarrow \mathrm{Ti(II)} + 2e^- \qquad (4)$$

according to Rossokhin *et al.* [7] and Baboian *et al.* [8]. This was also observed by Popov *et al.* [9] when oxidizing titanium in LiCl–KCl eutectic melts. However, oxidation of TiC was found to give stable Ti(III) species.

The solubility of $TiCl_4$ in alkali chlorides is, in most cases, very low, whereas $TiCl_2$ is soluble to varying degrees depending on composition and temperature. It has been demonstrated by several workers [10, 11] that an equilibrium exists between the three constituents (Ti, $TiCl_2$ and $TiCl_3$) and that the equilibrium

$$\mathrm{Ti} + 2\mathrm{Ti(III)} \rightleftharpoons 3\mathrm{Ti(II)} \qquad (5)$$

is displaced far to the right in most alkali chloride melts.

The kinetics of the reduction process has been studied by several workers. Quemper *et al.* [12] and Nardin *et al.* [13] recorded polarization curves showing several steps, which were attributed to Reactions 1-3. Babikhin and Makarov [14] conducted voltammetric studies in LiCl–KCl eutectic melts containing titanium chlorides. Reduction peaks and the corresponding oxidation peaks were observed which agreed with the proposed reaction scheme (Equations 1–3). Ferry *et al.* [15] carried out similar studies in the same systems, and peaks corresponding to Reactions 2 and

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3 were observed. The Ti(III)/Ti(II) couple was found to be quasi-reversible, while the Ti(II)/Ti(0) couple was irreversible.

The fact that titanium is present in different valency states involves the risk of red–ox, disproportionation and reoxidation reactions leading to severe losses in current efficiency. The use of various types of diaphragms to separate the anolyte and catholyte or circulation of the electrolyte between two separate cells have been proposed to solve this problem. In the latter case prereduction of Ti(IV) to Ti(II) is performed in one cell and reduction to metallic titanium in the other [16].

Titanium may be electrolytically deposited in the form of coherent deposits, dendritic or spongy crystals or powder. The nature of the deposit is dependent on several factors, such as temperature, melt composition, current density and substrate material. Most studies of titanium deposition have been performed in chloride melts containing $TiCl_3/TiCl_2$ and a soluble titanium anode. Experience has shown that the average valence of dissolved titanium chlorides should be close to 2.0 in order to get a good quality deposit. The presence of oxides or introduction of oxygen causes the valence to increase. High current densities approaching the limiting current density lead to powdery deposits. Electrolysis at high cathodic overvoltage may involve codeposition of alkali metals which react with titanium chlorides resulting in the formation of fines.

The purpose of the present work was to study the mechanism and the kinetics of electrodeposition of titanium from chloride melts and to study the nature of the deposits as a function of electrolyte composition, current density and temperature.

2. Experimental details

Most of the experiments were conducted in the KCl–LiCl eutectic mixture at 450° C. Some studies were made in the KCl–NaCl equimolar molten mixture, in KCl–LiCl–NaCl (40 : 20 : 40) and in NaCl. In the kinetic studies the titanium chloride concentration was varied from 0.5×10^{-4} to $3.0 \times 10^{-4}\,\mathrm{mol\,cm^{-3}}$ corresponding to 0.36–2.16 wt % calculated as $TiCl_2$. The temperature was varied in the range 450–800° C. $TiCl_3$ (+98%) was stored under argon atmosphere and used without further purification. The alkali chlorides were dried and purified using standard procedures. All handling of the chemicals was performed in a glove box with dry argon. Solid $TiCl_3$ was added to the melts in the presence of titanium foil to allow equation 5 to be established.

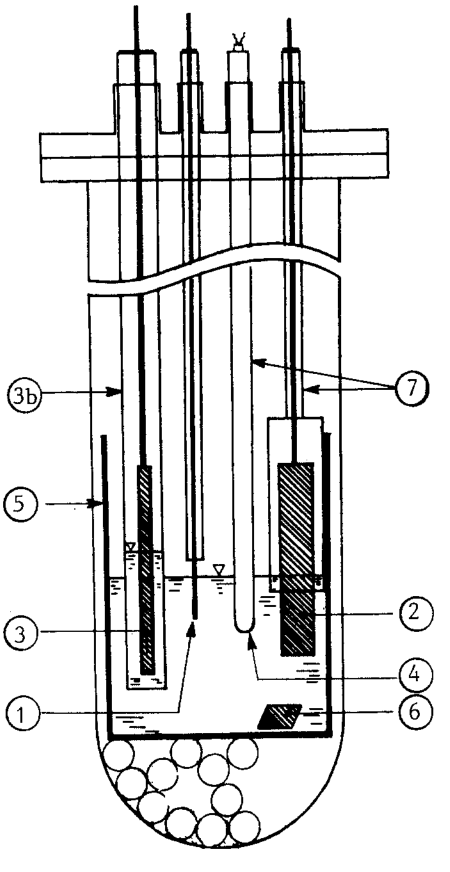

Fig. 1. The experimental cell. (1) Working electrode: stainless steel, iron, tungsten, (2) counter electrode: titanium, (3) reference electrode: titanium, (3b) reference electrode compartment (tube of Al_2O_3–SiO_2–Na_2O), (4) thermocouple, (5) alumina crucible, (6) excess titanium and (7) alumina tubes.

Polished rods of stainless steel, tungsten and iron were used as working electrodes. In some cases the electrode was sheathed with boron nitride. Titanium or graphite was used as the counter electrode while a titanium rod served as a reference electrode. The container material was either silica or alumina. A sketch of the experimental cell is shown in Fig. 1. The electrolytic deposition of titanium was studied by the potential step technique. To study the morphology of the deposits steady state electrolysis was performed in several electrolytes: KCl–LiCl eutectic, NaCl–KCl eutectic, KCl–LiCl–NaCl (40 : 20 : 40 mol%) and NaCl. The working electrodes were rods of stainless steel or tungsten, while the anode was titanium or graphite and a titanium rod served as reference electrode. The working temperatures ranged from 450 to 850° C. Most of the experiments were carried out at concentrations of about 5 wt% $TiCl_2$ and at current densities between 20 and $400\,\mathrm{mA\,cm^{-2}}$. The duration of each run ranged from several minutes up to about 20 h. In most of this work the anode was a consumable titanium electrode, but a chlorine evolving graphite anode was also used.

After cooling to room temperature, the entrained salt was leached from the cathode product in a 5% HCl solution. The deposits were inspected visually from optical and scanning electron micrographs.

3. Results and discussion

3.1. *General observations*

The potential between the titanium reference electrode and the working electrode became stable after a period of about two days after adding $TiCl_3$ and Ti, indicating that the following equilibrium

$$2TiCl_3 + Ti \rightleftharpoons 3TiCl_2 \qquad (6)$$

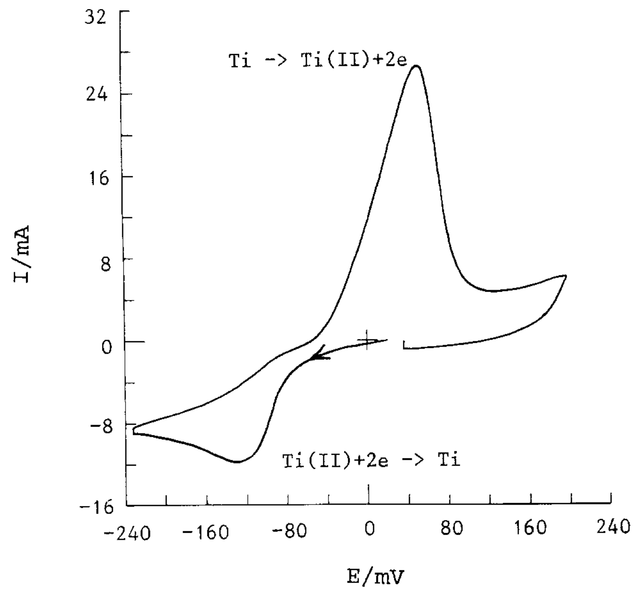

Fig. 2. Cyclic voltammogram obtained on a tungsten electrode showing the reduction of Ti(II) and the reoxidation of titanium to TiCl$_2$. KCl-LiCl eutectic at 455°C, [TiCl$_2$] = 1.0 × 10^{-4}-mol cm^{-3}, sweep rate = 10 mV s^{-1}, electrode area = 0.40cm^2.

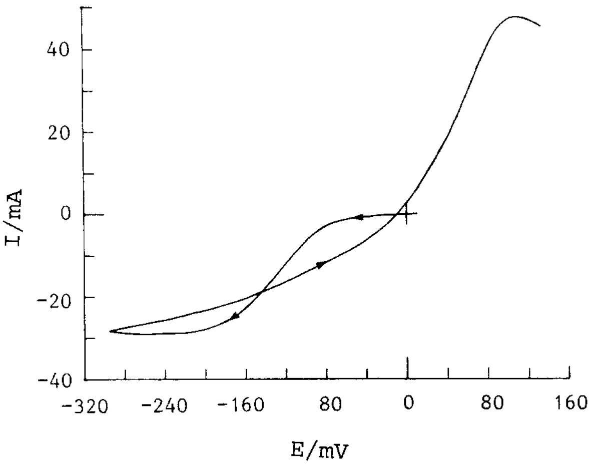

Fig. 3. Cyclic voltammogram illustrating the 'nucleation cross-over effect' on the return sweep for deposition of titanium on a tungsten substrate (0.40 cm^2). KCl-LiCl eutectic at 456° C, [TiCl$_2$] = 1.0 × 10^{-4} mol cm^{-3}, sweep rate = 200 mV s^{-1}.

was established. From literature studies [10, 11] the average valence of the titanium chlorides (TiCl$_x$) was expected to be close to 2. Preliminary valence studies and examination of the electrochemical results indicated that the actual magnitude of the valence could deviate considerably from this value. After several days the melt conditions deteriorated and lead to non-reproducible results. Particles floating in the melt and a black, metallic deposit on the walls of the container were observed after the experiments. This was believed to be titanium formed in disproportionation reactions, possibly involving the crucible materials.

3.2. *Voltammetry*

A typical voltammogram obtained on tungsten in KCl-LiCl at 450° C exhibiting reduction of Ti(II) and oxidation of titanium is given in Fig. 2. A considerable overpotential was observed when depositing titanium on a foreign substrate, such as tungsten. Evidence of the formation of a new phase is shown on the cyclic voltammetric response in Fig. 3. The cross-over of the current on the reverse sweep is typical for a process associated with nucleation.

The values of the cathodic peak potential, and the total peak separation (up to about 220 mV) were considerably larger than expected for reversible and purely diffusion controlled processes, indicating some irreversibility of the system Ti(II)/Ti(0). Diffusion controlled conditions could be obtained at a sweep rate as high as 50 V s^{-1}. Linear plots of the cathodic peak current versus the square root of the sweep rate are shown in Fig. 4. From the slope of such plots the diffusion coefficient of Ti(II) could be calculated.

Voltammetric studies performed in KCl-NaCl eutectic melt at temperatures above 700° C gave voltammograms very much like those obtained in KCl-LiCl. When the initial (starting) potential was extended beyond 300 mV a new distinct anodic peak occurred at + 300 mV, as shown in Fig. 5. This peak increased as the lower potential limit was lowered (more titanium deposited), indicating that this peak was dependent on the amount of Ti deposited and subsequently reoxidized.The peak was probably caused by the oxidation of Ti(II) to Tt(III), and the corresponding reduction of Ti(III) to Ti(II) then took place prior to the deposition peak.

The potential difference of the two red-ox systems Ti(III)/Ti(II) and Ti(II)/Ti was within the range of the values reported in the literature [8, 15].

The nature of the cathodic prewave appearing at about − 50 mV in the voltammograms in Fig. 5 is not quite clear. It appears to be a wave which is reduced to a shoulder in the presence of the metal deposition peak. However, this shoulder sometimes appeared as a fairly distinct peak during the initial period after adding Ti and TiCl$_3$. Voltammetric studies of this peak yielded a linear i_p–$v^{1/2}$ relationship indicating diffusion control under such conditions. At sweep rates above 50 mV s^{-1} the prepeak merged with the metal deposition peak. At the most, the magnitude of the peak current of the prepeak was 30–40% of the deposition peak current.

A characteristic feature of the prewave was the fact that when the potential during cyclic voltammetry was kept below the potential region of the Ti(II)/Ti(III) red–ox couple, the prewave did not appear at all. Evidently, the shoulder prior to the deposition peak should be associated with the reduction of Ti(III) to Ti(II) at the electrode surface.

From previous work [14, 15] it can be seen that the reduction of Ti(III) to Ti(II) appears as a wave prior to the metal deposition peak. The peak separation on the voltammogram presented by Balikhin and Makarov [14] is slightly above 200 mV (KCl–LiCl equimolar at 550° C), which is within the range of the results from the present work.

It appears that the reduction of Ti(III) to Ti(II) is very irreversible, and that it occurs over the whole potential range including peak B and the prepeak (at

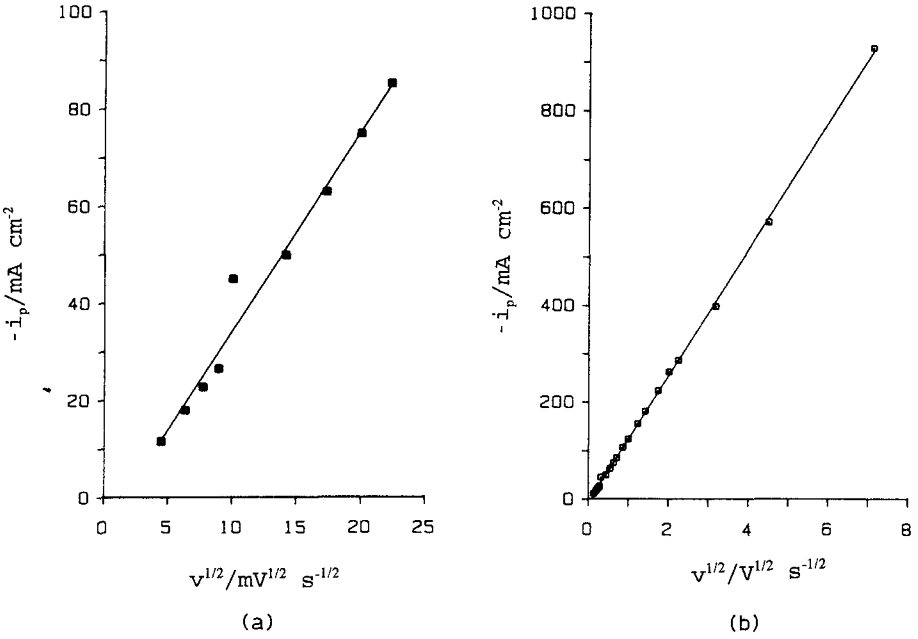

Fig. 4. Cathodic peak current against square root of sweep rate (range: a) below 0.6 V s^{-1}, b) 0.02 to 50 V s^{-1}). Stainless steel electrode, electrode area = 1 cm^2. KCl-LiCl eutectic with [TiCl$_2$] = 2.2 × 10^{-4} mol cm^{-3} at 484° C.

− 50 mV). The metal deposition peak (Ti(II) → Ti(0)) will be influenced by the extent of Ti(III) → Ti(II) reduction affecting the height of this peak (A).

3.3. *Chronoamperometry*

The current versus time responses from potential step experiments were used to study titanium deposition. The number of electrons transferred was determined to be close to the theoretical value of 2.0, confirming that the reaction under study was

$$Ti^{2+} + 2e^- \longrightarrow Ti \qquad (3)$$

The limiting current for this reaction was determined as a function of time in order to calculate the diffusion coefficient of the Ti(II) species.

Figure 6 shows a linear plot of the limiting current density in KCl-LiCl at 450° C against the inverse square root of time.

3.4. *The diffusion coefficient of the Ti(II) species*

The diffusion coefficient was determined to be 1.1 × 10^{-5} cm^2 s^{-1} (±25%) from voltammetry and

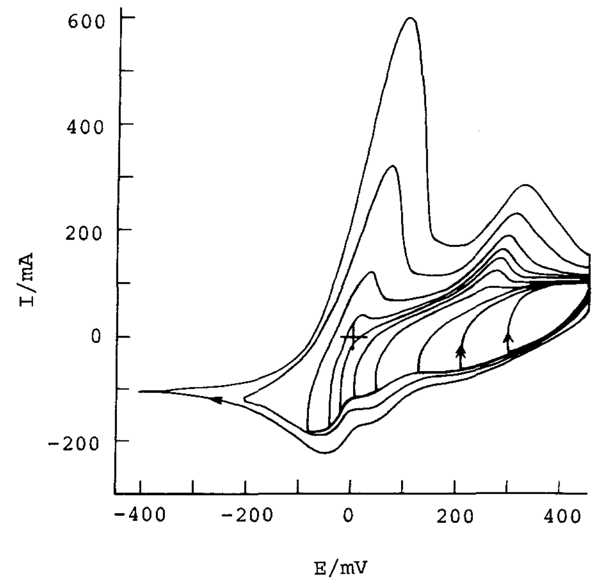

Fig. 5. Successive voltammograms with decreasing lower limit (more cathodic) obtained at a tungsten electrode (0.55 cm^2) in KCl-NaCl eutectic at 733° C. [TiCl$_2$] = 2.9 × 10^{-4} mol cm^{-3}, sweep rate = 50 mV s^{-1}.

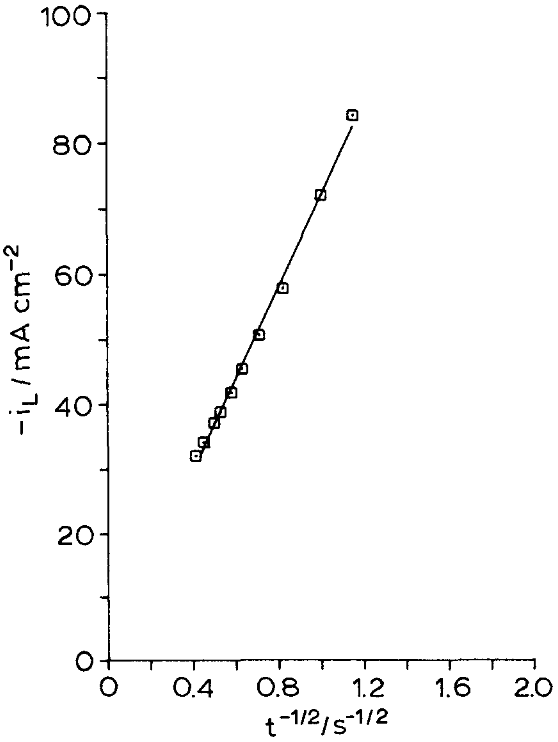

Fig. 6. Limiting current density versus the inverse square root of time from chronoamperometry in KCl-LiCl eutectic at 450° C, [TiCl$_2$] = 3.2 × 10^{-4} mol cm^{-3}, electrode area = 0.40 cm^2, E_{init} = + 30 mV.

Table 1. The diffusion coefficient of $TiCl_2$ at different temperatures determined by voltammetry and chronoamperometry. Tungsten electrode, $[TiCl_2] = 1.0 \times 10^{-4} mol\,cm^{-3}$ at 456° C in KCl–LiCl eutectic

Temperature °C	*Diffusion coefficient,* $10^5 D/cm^2 s^{-1}$ *voltammetry*	*chronoamperometry*
456	1.15	1.03
486	1.79	1.41
511	3.36	1.76
534	3.95	2.69
573	6.25	3.61
598	7.59	3.58

potential step experiments in KCl–LiCl eutectic melt at 450° C. The results from voltammetry gave slightly higher values than chronoamperometry. The temperature dependence of the diffusion coefficient was studied in the rather narrow range of 456–598° C. The corresponding activation energy of diffusion was found to be about $50\,kJ\,mol^{-1}$, which is close to the value of $58\,kJ\,mol^{-1}$, reported by Balikhin and Makarov [14] for the same melt. Numerical values are given in Table 1.

The diffusion coefficients determined from the voltammetric studies increased more rapidly with temperature, probably due to a rise in the background current as the temperature increased. The data from the potential step measurements were corrected by extrapolating the initial portion of the I–E curve using it as the baseline, so that they exhibited linear I–$t^{-1/2}$ relations with intercepts close to the origin.

Uncorrected voltammetric data resulted in linear $v^{1/2} - i_p$ plots which exhibited positive intercepts on the i_p axis. No proper method was found for correcting the i_p values. However, the background current was more pronounced in the case of chronoamperometry.

The diffusion coefficients given in Table 1 were calculated assuming that all dissolved titanium chloride was present as $TiCl_2$. There are, however, reasons to believe that the average valency of titanium ions in the melt was closer to 2.2 than to the assumed value of 2.0. Indications of the presence of $TiCl_3$ come from chemical analysis of melt samples and from the shape of voltammograms and results obtained from chronoamperometry. Correction for the presence of $TiCl_3$ would lead to somewhat higher diffusion coefficients.

In addition to the effect of the valence, the influence of background current due to the irreversible reduction of Ti(III) to Ti(II) may introduce error when calculating the diffusion coefficient.

Another factor influencing the accuracy of the calculated diffusion coefficient is related to the determination of the active area of the electrode. The area was determined by changing the depth of immersion in the electrolyte during voltammetry at constant sweep rate. The accuracy of the determination of the area was usually better than 8%.

The value of the diffusion coefficient obtained agreed well with the values cited from the literature as can be seen from Table 2. The diffusion coefficient obtained by Filippova and Baraboshkin [17] at 500° C is within the range obtained in the present work. The result due to Balikhin and Makarov [14] is also in agreement with the present work, while the conformity with the result of Vire [18] obtained at 550° C, depends on the magnitude of the activation energy of diffusion.

3.5. *Reaction kinetics*

The diffusion coefficients reported above were obtained from voltammograms recorded at low sweep rates. Plots of i_p against $v^{1/2}$ showed good approximation to linearity for sweep rates up to about $1000\,mV\,s^{-1}$. At higher sweep rates the slope of the i_p–$v^{1/2}$ plots decayed with increasing v, and the behaviour seemed to become quasi-reversible. The element of irreversibility was also proved by a shift in E_p as the sweep rate increased.

The heterogeneous reaction of electrodeposition of titanium is thought to exhibit mixed control when the rate of mass transport is high. Thus, in relatively slow kinetic studies, the reduction of Ti(II) becomes diffusion controlled.

Chronocoulometry and chronoamperometry at short times were applied in order to determine the rate constant for the charge transfer reaction for titanium deposition. The results suggest a value as low as 10^{-2}–$5 \times 10^{-3}\,cm\,s^{-1}$. However, purely irreversible behaviour was never observed. Far lower rate constants of the order of $10^{-6}\,cm\,s^{-1}$ have been reported by Ferry *et al.* [15] and by Popov *et al.* [19].

3.6. *Electrochemical nucleation*

Transients typical of a diffusion controlled process, i.e. linear I–$t^{-1/2}$ relations were obtained at low overpotentials in KCl–LiCl eutectic. As the steps were increased to an overpotential of about $-300\,mV$, a significant change in the I–t transients occurred, as shown in Fig. 7. After the initial double layer charging, the current dropped to a minimum and then rose with time. At even more negative overpotentials the current still passed through a minimum, and then a maximum, before finally decaying in the usual way with time.

The appearance of the I–t transients indicated that nucleation and growth phenomena play a part in the overall deposition process. After every run the deposited titanium was removed from the surface by polarizing the working electrode anodically. The rising part of the cathodic I–t transients obeyed an I against $t^{1/2}$ linear relationship according to the equation [20]

$$I = \pi z F (2DC)^{3/2} M^{1/2} t^{1/2} N \rho^{-1/2} \qquad (7)$$

as shown in Fig. 8. This demonstrates that instantaneous nucleation occurred at the surface of the substrate.

The nucleation phenomenon was difficult to detect

Table 2. Literature data on values of the diffusion coefficient of $TiCl_2$ obtained in previous investigations

Temperature/°C	*Diffusion coefficient × 10^5 /$cm^2 s^{-1}$*	*Standard rate constant × 10^6/$cm s^{-1}$*	*Reference*
456	1.10	~5000	Present work
500	1.54		17
450	1.65		14
550	(5.28–5.78)		18
450	1.20	2.08	19
470		3 ± 1	15

at concentrations lower than a few weight percent $TiCl_2$. It was observed at temperatures as low as 450°C in KCl-LiCl eutectic ($[TiCl_2] = 3.2 \times 10^{-4}$ mol cm^{-3} or 2.3 wt%) on tungsten electrodes. At low concentrations of $TiCl_2$ in the solution the overpotentials had to be increased in order to obtain transients indicating nucleation. At concentrations below about 1×10^{-4} mol cm^{-3} (0.72 wt% $TiCl_2$) transients characteristic for diffusion control were observed only, even at overpotentials larger than -1 V. At low concentrations the diffusion control seemed to suppress the appearance of the characteristics of the nucleation.

At higher concentrations the nucleation phenomenon would be expected to dominate prior to the onset of diffusion control, i.e. nucleation behaviour at low overpotentials and diffusion control at high overpotentials. In the present case these two events occurred in the reverse order; at low overpotentials diffusion control was observed, and if the concentration of $TiCl_2$ was high enough, the nucleation phenomenon appeared at higher overpotentials (-200 mV and more cathodic) followed by diffusion control.

A few seconds after the current maximum was reached, the curves shown in Fig. 7 exhibited a linear I against $t^{-1/2}$ relationship showing that diffusion control took over shortly after the initial nucleation. Long time behaviour of the current transients approached the limiting form for diffusion control, i.e. the Cotrell equation:

$$i = nFD^{1/2}c^0(\pi t)^{-1/2} \qquad (8)$$

Several diagnostic criteria have been developed [20] for testing current transients with respect to the nucleation mechanisms. The products of current and time at the current maxima were evaluated. The product $I_m t_m$ was found to decrease rapidly with increasing overpotential, while the product $I_m^2 t_m$ showed a stable value. This indicates that the growth was governed by three dimensional nucleation. However, a diffusion coefficient of reasonable magnitude could not be accurately determined from the following

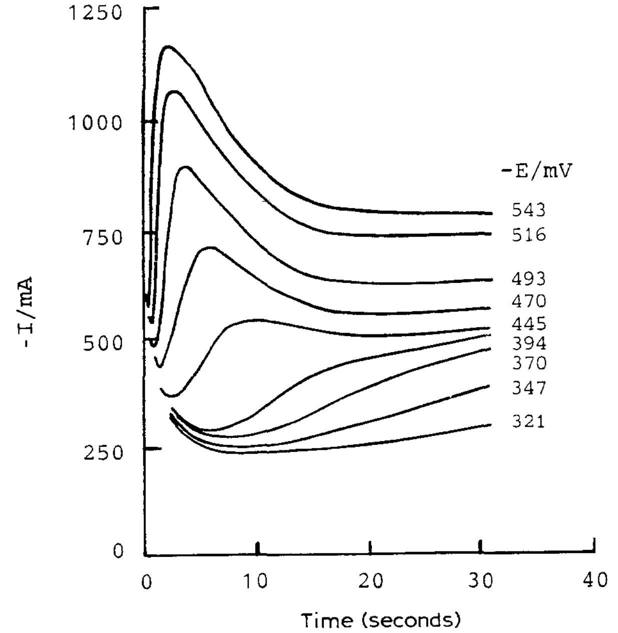

Fig. 7. Potentiostatic current transients for electrochemical deposition of titanium on a stainless steel electrode in KCl-LiCl eutectic at 602°C. $[TiCl_2] = 3.8 \pm 0.5$ wt% (5.2×10^{-4} mol cm^{-3} ± 15%), electrode area = 1.5 cm^2, $E_{init} = +10$ mV against Ti reference electrode. The potential steps are indicated on the curves.

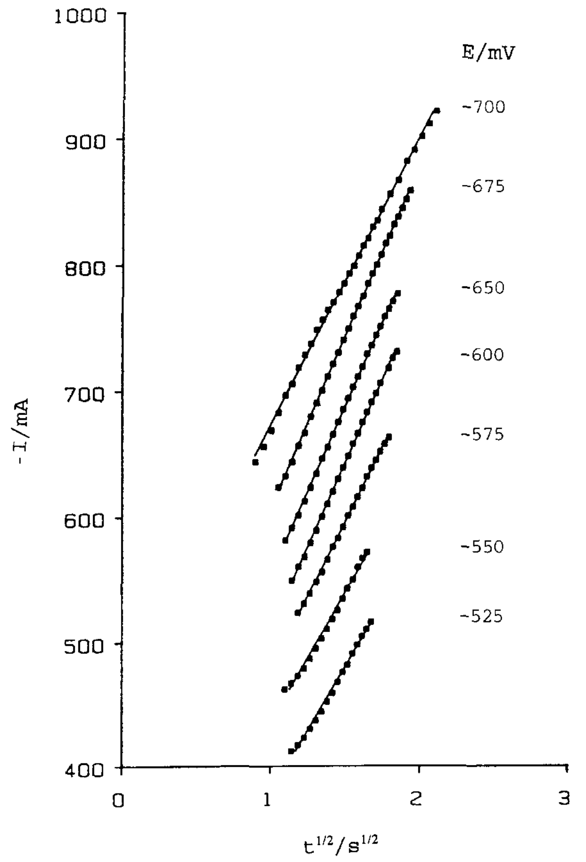

Fig. 8. Cathodic current against square root of time for the rising part of the potentiostatic current transients (numbers referring to potential steps). KCl-LiCl eutectic with 3 wt% $TiCl_2$ at 630°C, stainless steel cathode with area 0.9 cm^2.

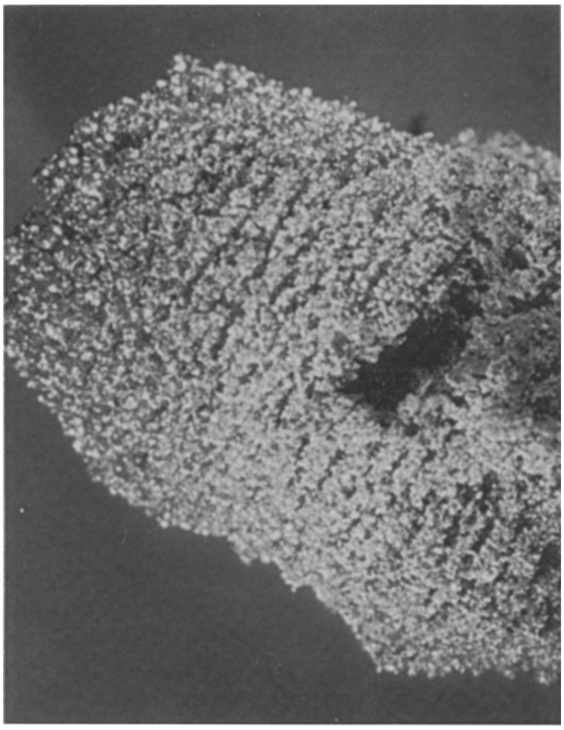

Fig. 9. Micrograph (× 12) showing titanium deposited under potentiostatic conditions (−100 mV) in KCl–LiCl eutectic with 1.6 wt % $TiCl_2$ at 450° C.

equation [20]

$$I_m^2 t_m = 0.163\,(nFc^0)^2 D \qquad (9)$$

Current-time transients obtained on tungsten electrodes in KCl–NaCl eutectic also showed evidence of nucleation processes. Examination of the region prior to the current maximum showed that it was difficult to distinguish between instantaneous and progressive nucleation in this case.

Electrodeposition of chromium from molten chlorides was studied by Vargas and Inman [21]. The results indicated progressive nucleation and three dimensional growth for the case of chromium deposition on tungsten.

3.7. *Studies of the crystal growth of titanium at constant current*

Initial attempts to electrodeposit titanium were made under constant potential conditions. At an overpotential of about −100 mV a thick deposit was obtained (see Fig. 9) in KCl–LiCl eutectic at 450° C and 1.6 wt% $TiCl_2$. Crystals larger than 10 μm constituted nodules with a size of several 100 μm with crystal faces somewhat rounded. The surface coverage and the adherence to the substrate was good. Due to the porous morphology, the deposit broke up into pieces when leaching out the entrained salt with hydrochloric acid. Vigorous gas evolution occurred due to oxidation of Ti(II).

A more fruitful approach to the study of the growth of titanium was to apply constant current in order to control the rate of deposition.

In molten KCl–LiCl cds ranging from 60 to 120 mA cm^{-2} seemed to be the most favourable, yielding coherent deposits with good surface coverage and adherence. At higher cds, the formation of dendrites was observed. High temperature favoured formation of large and bright crystals. At 450° C a thin film of Ti consisting of crystals smaller than 1 μm was formed initially on the electrode surface. Application of one or several initial high current pulses was found to improve the coverage, which is in accordance with experiments on chromium deposition from chloride melts reported by Vargas and Inman [21].

In NaCl–KCl eutectic at about 700° C a characteristic feature of the deposit was the growth of even-sized crystals all over the cathode. The drag out of salt was observed to be relatively high in the KCl–LiCl melt at 450° C, whereas NaCl at 850° C gave very little solidified melt adhering to the metal deposit.

The current efficiency (CE) was low, usually not better than 35%. Loss of metal particles from the cathode probably contributed to these low values. At high current density (400 mA cm^{-2}) the CE sometimes reached 90%. Experiments in KCl–NaCl demonstrated a slight tendency for the CE to increase with increasing temperature. The reproducibility of CE determinations became poor after the melt was used for more than one week. The calculation of CE was based on the reduction of Ti(II) only. If reduction of Ti(III) occurred simultaneously, the calculated values of CE are too low. Analysis of melt samples showed that the average valence of dissolved titanium chlorides tended to be higher than 2.2, indicating that some reduction of Ti(III) was likely to occur.

3.8. *Electrolysis using an insoluble anode*

When a graphite rod was used as anode, chlorine gas was evolved. The studies were performed in a quartz tube inside a transparent 'gold film furnace'. A nickel 0.16 mm mesh diaphragm surrounded the anode. The evolution of chlorine seemed to have a purifying effect on the melt. It allowed visual observation and inspection of the electrolyte during the whole period of the experiment. With a soluble titanium anode this was impossible because the electrolyte apparently turned black shortly after Ti + $TiCl_3$ was added.

At high cathodic overpotentials (−1000 mV) dark clouds formed at the cathode and they seemed to flow downwards from the cathode. This 'fog' was probably due to the formation of alkali metal at the cathode. At normal overpotentials the electrolyte remained transparent, and several colour changes were observed. Initially, a blue colour was observed in the zone close to the diaphragm and in the lower part of the melt, while the upper part and the vicinity of the cathode assumed a green colour. These two different colours persisted for some hours until the bulk of the electrolyte acquired a homogeneous green colour. In the cases where no diaphragm was employed, a layer at the electrolyte surface usually turned yellowish. The appearance of the blue colour in the melt was also observed during relatively strong chlorine evolution at the anode when no diaphragm was employed.

It has been fairly well established that the green colour is due to Ti(II) [8], while the blue colour has not been reported previously. In all likelihood it is due to Ti(III), although a purple colour has also been attributed to the oxidation of Ti(II) to Ti(III) [22, 23]. The pale yellow colour may be due to Ti(IV) [24, 25] but more likely it is caused by dissolved chlorine [26].

3.9. *The formation of a sludge*

From the very beginning of an experiment (after the addition of $TiCl_3$ + Ti) a dark non-transparent layer appeared at the bottom of the crucible, and it seemed to grow with time. If this layer was stirred the whole melt would turn dark. When the stirring was stopped, two layers consisting of the clear, green melt and black sludge at the bottom gradually reappeared. If the electrolysis current was interrupted, the melt slowly turned black, and it cleared again when electrolysis was resumed. Chemical analysis of samples taken from the bottom of the melt (the dark layer) showed $TiCl_x$ contents that were 3–15 times larger than that of the bulk of the melt (the green coloured segment). Concentrations up to 7.2 wt% $TiCl_x$ (calculated as $TiCl_2$) were determined for the bottom layer, while the bulk contained no more than 2 wt%. The samples from the lower part of the electrolyte usually contained black particles which did not dissolve in the HCl solution.

The sludge is believed to be composed mainly of electrolyte intermixed with metallic titanium formed partly by disproportionation of the melt, for example

$$3TiCl_2 = 2TiCl_3 + Ti \qquad (10)$$

and partly by titanium particles being detached from the cathode. The cathodic deposits were often spongy and a certain loss of material was likely to occur.

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