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Electrochemical studies of titanium in fluoride–chloride molten salts

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The interaction between titanium and Ti^{4+} ions (K_2TiF_6), the electroreduction reaction of Ti^{4+} ions and the anodic reaction of Ti in KCl–NaCl–KF melts with K_2TiF_6 at 973 K were studied by means of electrochemical and physical measurements. It was found that the fluoride ions played a very important role in these reactions

In KCl–NaCl–3 wt % K_2TiF_6 molten salts with less than 3 wt % KF, the interaction reaction was considered to proceed as $Ti^{4+} + Ti = 2Ti^{2+}$. If the bath contained more than 10 wt % KF, the reaction $3Ti^{4+} + Ti = 4Ti^{3+}$ occurred.

The electrochemical reduction of Ti^{4+} (K_2TiF_6) ions in the molten salts with less fluoride ions was observed to proceed according to three reaction steps, i.e. $Ti^{4+} + e = Ti^{3+}$, $Ti^{3+} + e = Ti^{2+}$, $Ti^{2+} + 2e = Ti$. In the case of the fluoride ion concentration being higher, two reduction steps, i.e. $Ti^{4+} + e = Ti^{3+}$, $Ti^{3+} + 3e = Ti$ were suggested.

1. Introduction

The electroreduction mechanism of Ti^{3+} ions in molten alkali chlorides has previously been studied by several workers [1–6]. Two reduction steps, i.e. $Ti^{3+} + e = Ti^{2+}$ and $Ti^{2+} + 2e = Ti$, have been observed.

The behaviour of Ti^{4+}(K_2TiF_6) in fluoride or chloride–fluoride molten salts has also been investigated in the literature [7–11]. It has been proposed that the reduction of Ti^{4+} ions in the molten salts proceeded in a two step process: i.e. $Ti^{4+} + e = Ti^{3+}$, $Ti^{3+} + 3e = Ti$. No existence of the intermediate reaction involving Ti^{2+} was observed.

In our previous paper [12], the reaction between titanium metal and Ti ions in equimolar KCl–NaCl melts with $TiCl_3$ or K_2TiF_6 at 973 K was investigated. It was found that the reaction in the molten melts with $TiCl_3$ proceeded according to $2Ti^{3+} + Ti = 3Ti^{2+}$. However, the reaction was more complex in the bath with K_2TiF_6 than that in the case of $TiCl_3$. The reaction was $Ti^{4+} + Ti = 2Ti^{2+}$, in KCl–NaCl melts with the concentration of less than 3 wt % K_2TiF_6 and $3Ti^{4+} + Ti = 4Ti^{3+}$ in the case of the concentration being higher than 9 wt %. The reaction of Ti in chloride–fluoride melts was affected by fluoride ions. In this paper, we describe the effects of fluoride ions on the reaction of Ti and the electroreduction behaviour of Ti^{4+}(K_2TiF_6) with addition of KF to KCl–NaCl–3 wt % or 10 wt % K_2TiF_6 melts by means of electrochemical and physical measurements.

2. Experimental details

The same experimental cell as in our previous paper [12] was used. All experiments were performed in a protective purified Ar atmosphere at 973 K.

The cathode used in these experiments was a Ti or a Pt electrode with a diameter of 1.6 mm or 0.5 mm. The counter electrode was a Pt wire with a much larger surface area. The reference electrode was Ag/AgCl(0.1 N) in an equimolar KCl–NaCl melt which was placed in a very thin mullite tube (Φ4 mm). This kind of reference electrode gave good stability and reproducible behaviour. The Ti plates of dimensions 10 × 10 × 2 mm were immersed in the molten salts for Ti weight change measurements.

An equimolar KCl–NaCl mixture was heated to its melting point, then cooled under a highly pure argon atmosphere to eliminate the moisture. The equimolar KCl–NaCl salt prepared in this way was chosen as the solvent. High purity K_2TiF_6 was used for the solute. KF was added to the bath to study the effects of fluoride ions on the reaction between Ti metal and Ti^{4+}(K_2TiF_6) and the electroreduction mechanism of Ti^{4+} in the molten salts.

3. Results and discussion

3.1. *The Ti weight changes associated with reaction between Ti and Ti^{4+} ions in the molten salts*

Fig. 1 presents the time dependence of the weight changes of Ti plates in KCl–NaCl–3 wt % (0.9 g) K_2TiF_6 molten salts with KF (0 or 23.3 wt %) at 973 K in an Ar protective atmosphere. The dashed lines represented the theoretical Ti weight changes according to various possible reactions. From this figure, it can be seen that the Ti weight changes increased with time initially. After about 3 h, a steady state was

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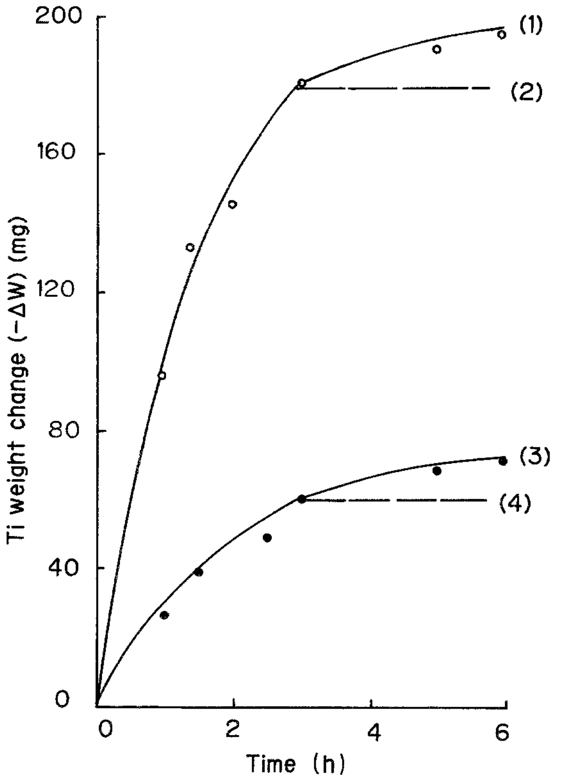

Fig. 1. Ti weight changes with time in KCl–NaCl–3 wt % K_2TiF_6 (0.9 g)–KF [(1) 0 wt %; (3) 23.3 wt %] at 700° C. Size of Ti plate: 5 × 5 × 2 mm. The dashed lines represent the theoretical Ti weight changes calculated from reactions; (2) $Ti^{4+} + Ti = 2Ti^{2+}$ and (4) $3Ti^{4+} + Ti = 4Ti^{3+}$.

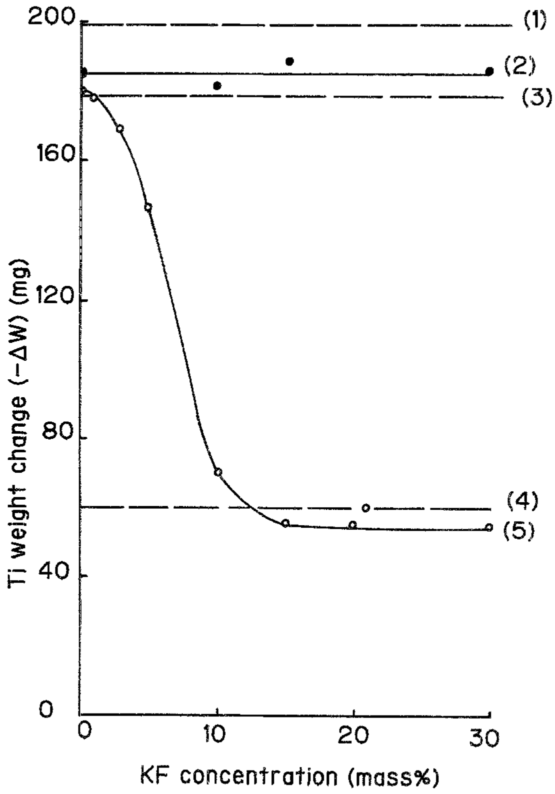

Fig. 2. Effects of KF concentration on the weight changes of Ti specimens immersed in KCl–NaCl–KF melts (30 g) with K_2TiF_6: (5) 3 wt %; (2) 10 wt % for 3 h. The dotted lines present the theoretical Ti weight changes deduced from reactions: $Ti^{4+} + Ti = 2Ti^{2+}$ [(3) 3 wt % K_2TiF_6]; $3Ti^{4+} + Ti = 4Ti^{3+}$ [(1) 10 wt % K_2TiF_6; (4) 3 wt % K_2TiF_6].

reached, i.e. the equilibrium of the reaction was obtained in 3 h. So, this reaction time of 3 h was chosen to determine the equilibrium Ti weight changes associated with the reaction between Ti and Ti^{4+} ions.

The equilibrium Ti weight changes as a function of KF concentrations in the molten salts with K_2TiF_6 are demonstrated in Fig. 2. The dashed lines in this figure represent the theoretical weight changes calculated according to various possible mechanisms assuming that these reactions proceed completely.

The Ti weight changes associated with the reaction between Ti metal and KCl–NaCl–3 wt % K_2TiF_6 melts with less than 3 wt % KF were in good agreement with the theoretical values calculated by reaction (1)

$$Ti^{4+} + Ti = 2\,Ti^{2+} \qquad (1)$$

The weight changes decreased with the KF concentrations in the concentration range 3–10 wt % KF, then became constant, i.e. the reaction appeared to proceed according to the following reaction

$$3\,Ti^{4+} + Ti = 4\,Ti^{3+} \qquad (2)$$

in the molten salts with higher than 10 wt % KF. It is suggested that the reaction involves both reactions (1) and (2) which reach equilibrium in KF concentrations of 3–10 wt %.

In KCl–NaCl–10 wt % K_2TiF_6 melts with various compositions of KF, the Ti weight changes were independent of the KF concentration. These values agreed approximately with the theoretical values obtained by reaction (2).

It can be concluded that the reaction between Ti and Ti^{4+} ions is similar to that in alkali chloride melts, if the fluoride–chloride mixed melts contain less fluoride ions. Otherwise, it is similar to that in fluoride molten salts, if the F^- ion concentration is higher. There also exists an intermediate fluoride ion concentration range in which reactions (1) and (2) occur simultaneously.

3.2. *Electroreduction of Ti^{4+} ions and anodic reaction of a Ti electrode*

In Section 3.1, we have described the behaviour of the reaction between Ti metal and Ti ions in KCl–NaCl–KF molten salts with K_2TiF_6 and the effects of fluoride ions on the reaction. It was observed that the fluoride ions played an important role in the reaction. In this section, the cathodic characteristics of Ti^{4+} ions (K_2TiF_6) and the anodic reaction of Ti metal will be discussed.

3.2.1. The electrochemical reaction in chloride–fluoride melts with lower concentration of fluoride ions. Typical linear voltammograms for the electroreduction of Ti^{4+} ions in KCl–NaCl–3 wt % K_2TiF_6 melts and the anodic reaction behaviour of Ti metal in pure KCl–NaCl molten salts are depicted in Fig. 3. Curve (1) in this figure demonstrates the cathodic current density-potential curve for the reduction of Ti^{4+} ions on a Pt electrode. Comparison of this result with that

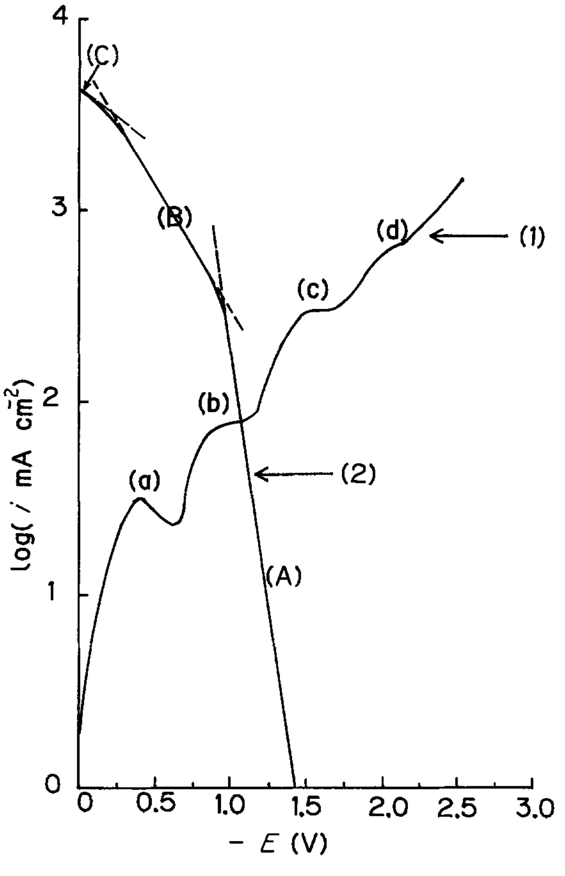

Fig. 3. (1) Cathodic polarization curve for reduction of Ti^{4+} ions in KCl–NaCl–3 wt % K_2TiF_6 molten salts; (2) Anodic polarization for Ti electrode in KCl–NaCl at 973 K. Scan rate: 50 mV sec^{-1}.

obtained in pure KCl–NaCl melts at a Pt electrode indicated that the current increase from potentials less than −2.0 was associated with the deposition of alkali metal. The reduction process of Ti^{4+} ions in the molten salts under study consisted of four steps. This differed from the results in the literature [7–11] where it was suggested that the reduction of Ti^{4+} ions in molten fluorides or chloride–fluorides was composed of two steps: $Ti^{4+} + e = Ti^{3+}$, $Ti^{3+} + 3e = Ti$. In this experiment, it was observed that the peak potentials were independent of the potential sweep rate and the peak current of peak (a) was linear with the square root of the sweep potential rate as depicted in Fig. 4.

Curve (2) in Fig. 3 represents the anodic behaviour of Ti metal in pure KCl–NaCl melts. It may be approximated by three different linear relations between log(i) and potential ($-E$). According to the standard potentials of the Ti/Ti^{4+}, Ti/Ti^{3+} and Ti/Ti^{2+} systems [17] in equimolar KCl–NaCl molten salts, it was considered that the curve is associated with the following three anodic reactions.

$$\text{(A)}\ Ti = Ti^{2+} + 2e \qquad (3)$$

$$\text{(B)}\ Ti = Ti^{3+} + 3e \qquad (4)$$

$$\text{(C)}\ Ti = Ti^{4+} + 4e \qquad (5)$$

Also, it was noted that part (A) of the anodic curve intersected with part (B) of the cathodic curve (at this range, the cathodic reaction corresponds to $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti^{2+}$ as discussed later in this paper).

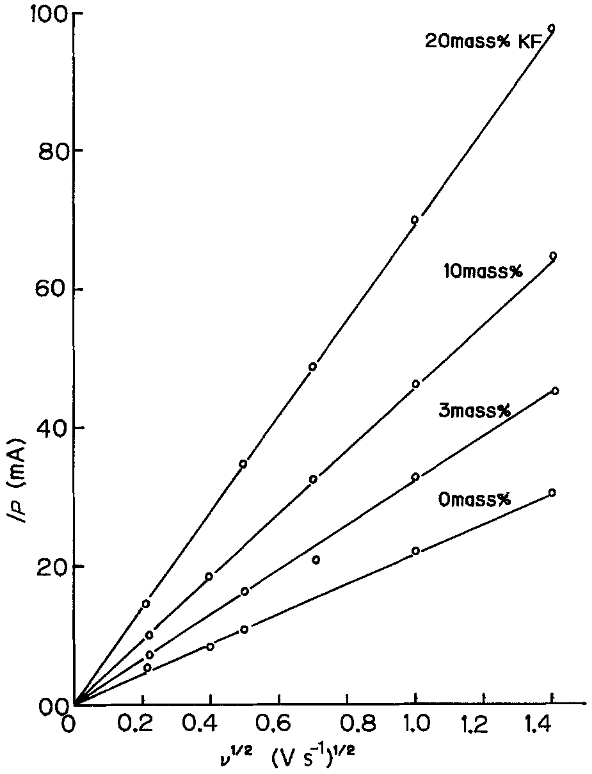

Fig. 4. Relation between Ip and $\nu^{1/2}$ for reduction of Ti^{4+} to Ti^{3+} in KCl–NaCl–3 wt % K_2TiF_6 molten salts with various KF concentrations at 973 K. Pt electrode = 0.159 cm^2.

The cyclic voltammogram of Ti^{4+} ions in KCl–NaCl melts with 3 wt % KF and K_2TiF_6 at 973 K showed three well defined peaks as shown in Fig. 5. The sweep rate was 1 V sec^{-1}. It was observed that the peak potentials were independent of the sweep rate

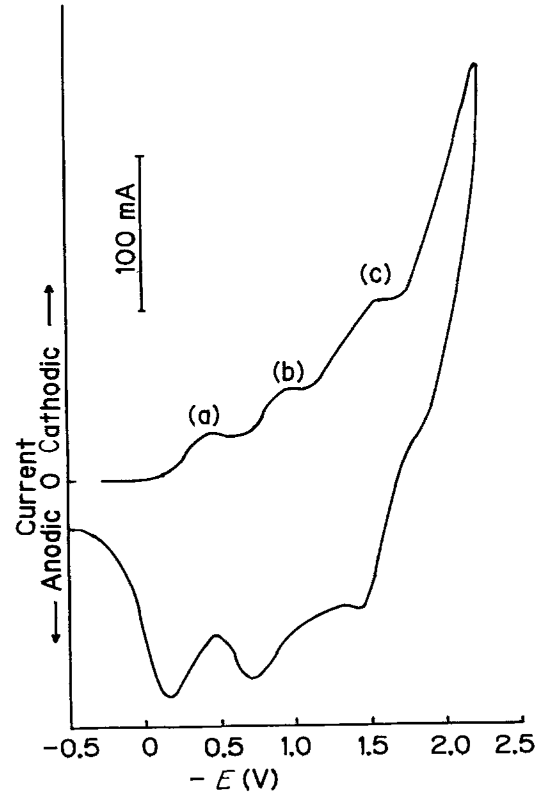

Fig. 5. Cyclic voltammetry for reduction of Ti^{4+} ions in KCl–NaCl–3 wt % K_2TiF_6–3 wt % KF melts. Pt electrode = 0.159 cm^2; scan rate = 1 V sec^{-1}; temperature = 973 K.

and the peak current of peak (a) in the molten salts was linear with the square root of the sweep rate. The peak (d) shown in Fig. 3 was not clear in this figure. It was probably due to the reduction of the alkali cation ions.

It is clear that the electroreduction of Ti^{4+} in KCl–NaCl–3 wt % K_2TiF_6 molten salts with KF less than 3 wt % on a Pt electrode is controlled by a simple (quasi) reversible charge transfer and diffusion mechanism.

For the estimation of the electron number involved in the electrochemical reduction of Ti^{4+} ions on a Pt electrode, the following equation can be used [13–16]:

$$E_{pa} - E_{pc} = E_{pc/2} - E_{pc} = 2.2\,RT/(nF) \quad (6)$$

where, E_{pa} is the anodic peak potential; E_{pc}, the cathodic peak potential; $E_{pc/2}$, the potential at $I = 0.5\,I_{pc}$; I_{pc}, the current at the cathodic peak potential; n, the electron number. According to this equation, the mean values for the number of electrons in the reduction steps are demonstrated in Table 1.

X-ray diffraction analysis was performed to identify the products formed at a Pt electrode under potential controlled electrolysis. Electrolysis at the potential corresponding to peak (a), (b) did not lead to the formation of a new phase in the cathode. During the potentiostatic electrolysis at the potential of -1.50 V corresponding to the peak (c) of the reduction, Pt–Ti alloy (PtTi, Pt_3Ti, $PtTi_3$) deposited on the cathode. When electrolysis at the potential of -1.90 V corresponding to peak (d) in Fig. 3 was performed, metallic titanium was also detected, besides the Pt–Ti alloy, according to X-ray diffraction analysis. Thus, taking into consideration the electron number in Table 1 and the X-ray diffraction data, it was proposed that the electrochemical reduction of Ti^{4+} ions in KCl–NaCl–3 wt % K_2TiF_6 melts with less KF than 3 wt % on a Pt electrode was a four step reduction process:

$$\text{(a)}\ Ti^{4+} + e = Ti^{3+} \quad (7)$$

$$\text{(b)}\ Ti^{3+} + e = Ti^{2+} \quad (8)$$

$$\text{(c)}\ Ti^{2+} + 2e = \text{Ti (Pt alloy)} \quad (9)$$

$$\text{(d)}\ Ti^{2+} + 2e = \text{Ti (pure)} \quad (10)$$

Thus, the intermediate reaction involving Ti^{2+} ions was observed in chloride–fluoride molten salts with less fluoride ions, although it was not observed by other workers [7–11] in fluoride–chloride molten salts.

3.2.2. The electrochemical reaction in the molten salts with higher concentration of fluoride ions. The reduction behaviour of Ti^{4+} ions and the anodic behaviour of Ti metal in the molten salts with higher concentration of K_2TiF_6 or KF have also been studied in this experiment to clarify the effects of F^- ions. Fig. 6 shows typical voltammograms for the reduction of Ti^{4+} on a Pt electrode in KCl–NaCl–3 wt % K_2TiF_6 melts with 10 wt % KF and the anodic reactions of a Ti electrode in KCl–NaCl molten salts with 10 wt % at 973 K. Curve (1) in this figure demonstrates the cathodic current density potential curve for the reduction of Ti^{4+} ions in the molten salts. In comparison of this curve to that shown in Fig. 3, it was observed that the reduction in these two cases appeared different. In this case as shown in Fig. 6, only three steps were observed. Also, the peak potentials for the steps did not change with potential sweep rate. Fig. 4 showed that the peak current was linear with the square root of the sweep rate. Thus, the reduction of Ti^{4+} ions in the molten salts with 10 wt % KF was also a simple charge transfer and diffusion controlled mechanism. The mean values of the electron number obtained by use of equation (6) are given in Table 1. The electron number was approximately equal to 1, 3, 3 for step (a), (c), (d), respectively. These results agreed well with those in the literature [7–11].

Table 1. The values of the electron numbers for the reduction of Ti^{4+} in KCl–NaCl–3 wt % K_2TiF_6 melts with various concentrations of KF

Reduction step	(*a*)	(*b*)	(*c*)	(*d*)
0 wt % KF	0.92	0.95	2.01	1.94
3 wt % KF	1.02	0.90	1.86	
10 wt % KF	1.01		2.99	
20 wt % KF	0.92		2.96	

Curve (2) in Fig. 6 is the anodic current–potential of a Ti electrode in KCl–NaCl melts with 10 wt % KF. It is similar to that given in Fig. 3. However, the poten-

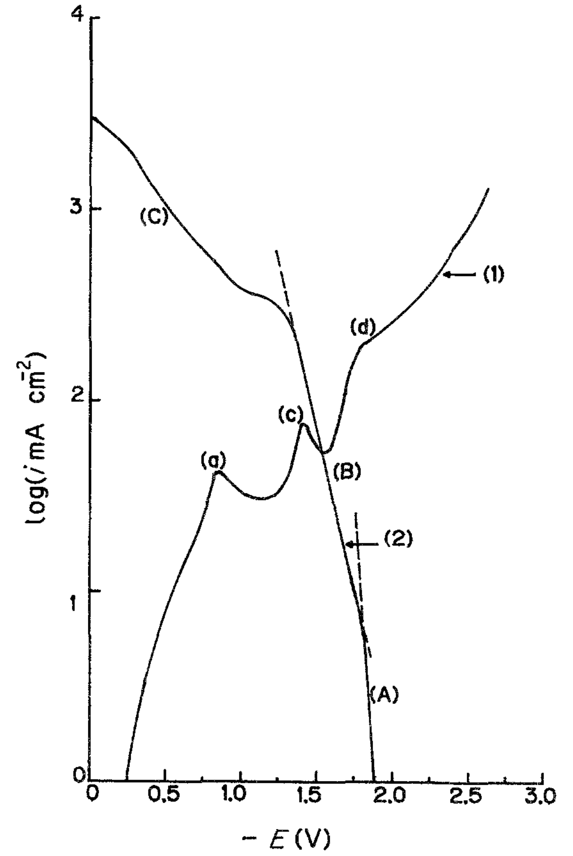

Fig. 6. (1) Cathodic polarization curve for reduction of Ti^{4+} ions in KCl–NaCl–3 wt % K_2TiF_6–10 wt % KF molten salts; (2) Anodic polarization for Ti electrode in KCl–NaCl–10 wt % KF at 973 K. Scan rate = 50 mV sec^{-1}.

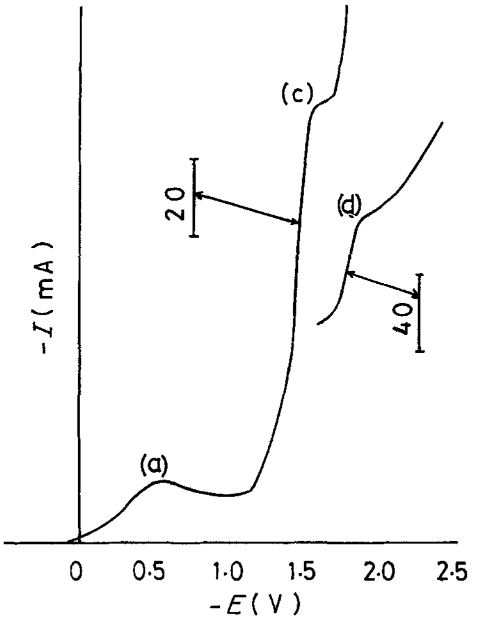

Fig. 7. Linear sweep voltammogram for reduction of Ti^{4+} ions in KCl–NaCl–10 wt % K_2TiF_6 molten salts at 973 K. Pt electrode surface area = 0.159 cm^2; scan rate = 50 mV sec^{-1}.

tial range for part (A) shifted to lower values with the concentration increase of KF in the bath gradually. It is the same for parts (B) and (C). This is probably due to the change of the complex state of Ti ions in the molten salts with different concentrations of fluoride ions as discussed in Section 3.1.

In Fig. 6, it was noted that part (B) of the anodic curve intersected with part (c) of the cathodic one. This point was different from that shown in Fig. 3.

A typical voltammogram for the reduction of Ti^{4+} ions in KCl–NaCl melts with 10 wt % K_2TiF_6 is shown in Fig. 7. Three peaks are observed in this case. By use of equation (6), the mean electron numbers are demonstrated in Table 2. The behaviour of Ti^{4+} ions was similar to that in KCl–NaCl–3 wt % K_2TiF_6 molten salts with 10 wt % KF shown in Fig. 6.

X-ray diffraction analysis was performed to clarify the nature of the products on the cathode. According to the data in Tables 1 and 2 and the X-ray diffraction measurements, the following three step process for the reduction of Ti^{4+} ions in KCl–NaCl melts with 10 wt % K_2TiF_6 and the molten salts with 3 wt % K_2TiF_6 and 10 wt % KF, was suggested:

$$\text{(a)}\quad Ti^{4+} + e = Ti^{3+} \tag{11}$$

$$\text{(c)}\quad Ti^{3+} + 3e = \text{Ti (Pt alloy)} \tag{12}$$

$$\text{(d)}\quad Ti^{3+} + 3e = \text{Ti (pure)} \tag{13}$$

that is in agreement with the data in earlier work [7–11].

Table 2. The values of n for the reduction of Ti^{4+} in KCl–NaCl–K_2TiF_6

Reduction step	(*a*)	(*b*)	(*c*)	(*d*)
10 wt %	1.01		2.82	3.02

3.2.3. The interaction between Ti and Ti^{4+} ions deduced from voltammograms. The reaction between Ti and Ti^{4+} ions in the molten salts with K_2TiF_6 may be discussed from the electrodic reactions taking place at the intersection point of the anodic and cathodic linear sweep voltammograms shown in Figs 3 and 6. The reaction of Ti with the molten salts can be divided into an anodic reaction and a cathodic reaction.

In KCl–NaCl molten salts with 3 wt % K_2TiF_6, the reaction can be obtained from the results shown in Fig. 3. Near the potential at the intersection point, the cathodic reaction consists of reactions (7) and (8). It is rewritten by the following reaction.

$$Ti^{4+} + 2e = Ti^{2+} \tag{14}$$

The anodic reaction is reaction (3). Taking into consideration reactions (14) and (3), the following reaction is deduced.

$$Ti + Ti^{4+} = 2Ti^{2+} \tag{15}$$

which is in agreement with that obtained by the Ti weight change measurements. Similarly, the reaction deduced according to the data in Fig. 6 is

$$Ti + 3Ti^{4+} = 4Ti^{3+} \tag{16}$$

for the reaction between Ti metal and Ti^{4+} ions in KCl–NaCl–3 wt % K_2TiF_6 melts with 10 wt % KF. It is obvious that reaction (16) is the same as reaction (2) in Section 3.1.

4. Conclusion

In molten chloride–fluorides the behaviour of titanium has been elucidated by use of various electrochemical and physical methods. Also, the effects of fluoride ions in the molten salts on the reaction between titanium and the melts with K_2TiF_6, the electrochemical reduction of Ti^{4+} ions and the anodic characteristic of a titanium electrode at 973 K, have been clarified. Different interaction mechanism and electrochemical reduction process of Ti^{4+} ions are suggested in the chloride–fluoride melts with lower or higher concentration of fluoride ions, respectively. There exists an intermediate reaction involving Ti^{2+} ions in the mixed melts, when the concentration of F^- ions is low.

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