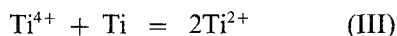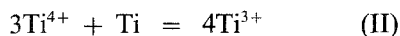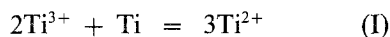# Electrochemical studies of the reaction between titanium metal and titanium ions in the KCl–NaCl molten salt system at 973 K

CHEN GUANG-SEN, MASAZUMI OKIDO, TAKEO OKI

Department of Metallurgy and Iron and Steel Engineering, Nagoya University, Nagoya, Japan

The reaction between titanium metal and titanium ions in the KCl–NaCl molten salt system was investigated by means of electrochemical and physical methods at 973 K in an inert gas atmosphere (argon). It was found that the reaction between titanium metal and Ti^{3+} in the molten salts with $TiCl_3$ followed a simple reaction (I). However, in the case of the concentration of K_2TiF_6 being higher than 2.7 mol % the reaction was (II); in the case of it being less than 0.8 mol %, reactions (III) and (III') were followed.

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

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

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

$$3Ti^{2+} = Ti + 2Ti^{3+} \qquad (III') \text{ (on cooling)}$$

It was also found that these reactions were controlled by charge transfer and diffusion simultaneously.

1. Introduction

The electrodeposition of titanium from molten salt systems has been investigated by many researchers [1–6]. However, the process is complicated by the lower valent compounds of titanium (Ti^{2+}, Ti^{3+}) which exist in the electrolytic bath as the result of the reactions between metallic titanium and tetra- or trivalent titanium ions [7–10]. There are currently a number of papers concerning the equilibrium between titanium metal and chloride molten salts containing high oxidation state titanium chloride, especially $TiCl_4$ or $TiCl_3$ [10–13], but few reports concerning the mechanism and kinetic behaviour of the interactions between titanium metal and titanium ions in various compositions. This is of importance, not only for the electrodeposition of titanium from molten salt systems, but also for studies on the formation of thin films, for example TiC which can be synthesized on iron, steel, or carbon by means of disproportionation

reactions in molten salts, and has valuable anti-corrosion properties, high hardness and good wear resistance [14]. It was the purpose of this paper to discuss the behaviour of the reaction between titanium metal and titanium ions in KCl–NaCl molten salts by electrochemical and physical analysis methods.

2. Experimental details

The experimental cell is shown in Fig. 1. All experiments were carried out in a protective purified argon atmosphere at a temperature of 973 ± 2 K. A system with three electrodes i.e. a reference electrode, a working electrode and a counter electrode, was used for the faradaic impedance measurements. The reference electrode was of silver–silver chloride, Ag–AgCl (0.1 N), in equimolar KCl–NaCl molten salt which was put into a very thin mullite alundam tube. The working electrode was a titanium electode or a platinum electrode which was prepared
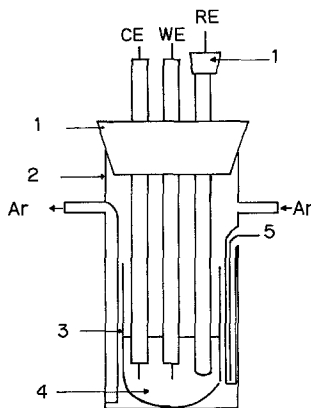
Fig. 1. Electrolysis cell with cylindrical geometry. WE, Working electrode (titanium or platinum); CE, counter electrode (platinum); RE, reference electrode (Ag/AgCl(0.1 N)–KCl–NaCl). 1, Silicone rubber; 2, quartz tube; 3, mullite crucible; 4, electrolyte; 5, thermocouple (CA).

stat. The faradaic impedance measurements were performed using a digital frequency response analyser [15] with superimposed alternate voltage, where an alternate ΔE_p of about $10\,mV$ amplitude peak-to-peak was used.

The titanium plates were immersed for 70 min in the molten salts which initially contained various compositions of K_2TiF_6. The titanium plates were taken out of the molten salts but were still kept in the electrolysis cell. The molten salts in the crucible were cooled in the inert atmosphere and solidified. The solidified salts were leached with boiled distilled water to dissolve the alkali chlorides and to concentrate the products formed by the reaction between titanium and Ti^{4+} ions (K_2TiF_6). During leaching of the solidified salts, no significant gas evolution occurred. The remaining materials were collected and used for the analyses of the products and then analysed by use of the standard procedures of X-ray diffraction using a Cu–$K\alpha$ anticathode to obtain information about the low-valency oxidation state of titanium directly or indirectly.

From the results published in the literature [16–19] it was observed that TiF_3, alkali titanium tri- or tetrafluoride (K_3TiF_6, K_2NaTiF_6, $KTiF_4$, K_2TiF_6 and so on) dissolved sparingly in water. Therefore, the products can be identified directly by X-ray diffraction analysis if they exist as titanium tri- or tetrafluoride compounds in the solidified salts. If the products are stable as (alkali) titanium difluoride or chloride in the solidified salts, (hydrogen) gas evolution can be observed during leaching. The products will be identified as only (alkali) titanium trifluorides because it is well known that Ti^{2+} ions are oxidized to Ti^{3+} ions by water with hydrogen gas evolution [16, 20]. Thus, X-ray diffraction can be used for the identification of the products after water leaching of the solidified salts.

from titanium wire of 1.6 mm diameter or platinum wire of 0.5 mm diameter and then sheathed in a mullite alundam tube and sealed with alumina cement. The surface area of the working electrode (titanium or platinum was $0.523\,cm^2$ or $0.159\,cm^2$, respectively. The counter electrode was platinum wire with a large surface area prepared in the same way as the working electrode. The titanium plate of $10 \times 10 \times 2\,mm$ was immersed in the molten salts for 70 min for measurements of weight change.

An equimolar KCl–NaCl mixture was used as supporting electrolyte. This was prepared from commercial alkali halides of high chemical purity, heated to their melting point in a vacuum so that they contained negligible moisture. To give titanium ions, chemical purity K_2TiF_6 and $TiCl_3$ were both used. The relation between the initial amount and mol % of K_2TiF_6 or $TiCl_3$ in the molten salts is given in Table 1. The wt % of K_2TiF_6 or $TiCl_3$ in the molten salts can be easily calculated by changing moles into weight.

Potentiostatic or galvanostatic control was achieved by means of a conventional potentio-

Table 1. Relation between initial moles and mol % of K_2TiF_6 or $TiCl_3$ in KCl–NaCl (15 g) molten salts used in this work

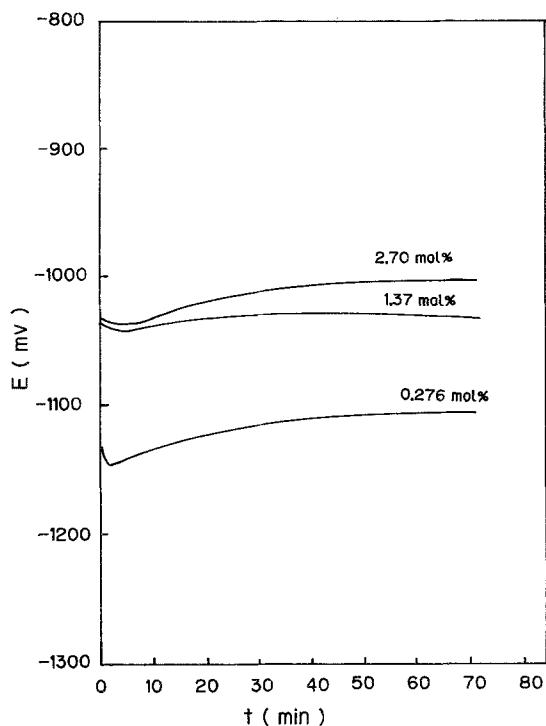|						
K_2TiF_6 (mol $\times 10^{-3}$)	0.625	1.874	3.124	4.373	6.248	9.372
K_2TiF_6 (mol %)	0.276	0.817	1.370	1.901	2.702	3.994
$TiCl_3$ (mol $\times 10^{-3}$)	0.625	1.874	3.124	4.373	6.248	9.372
$TiCl_3$ (mol %)	0.276	0.817	1.370	1.901	2.702	3.994

Fig. 2. Time dependence of mixed potential of titanium plate in KCl–NaCl molten salts containing various compositions of TiCl₃ at 973 K.
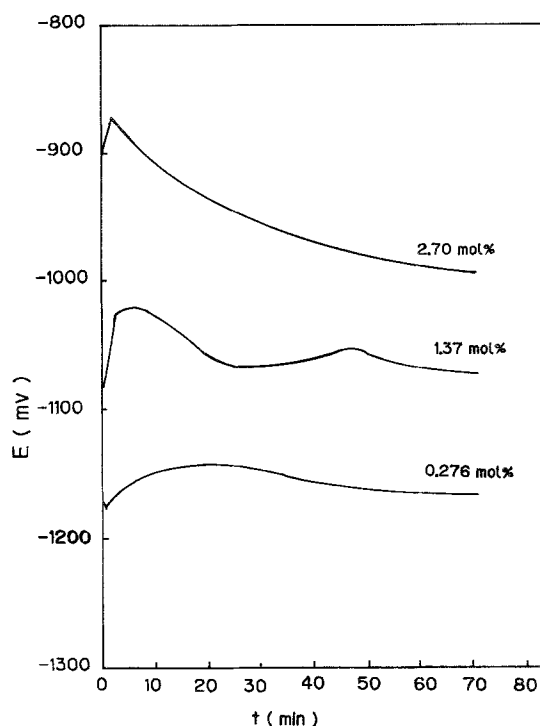
Fig. 3. Time dependence of mixed potential of titanium plate in KCl–NaCl molten salts containing various compositions of K_2TiF_6 at 973 K.

3. Results

3.1. *Mixed potential and weight change of titanium metal in equimolar KCl–NaCl molten salts containing $TiCl_3$ or K_2TiF_6*

Typical mixed potential versus time curves for titanium metal in KCl–NaCl containing $TiCl_3$ are shown in Fig. 2 (at 973 K at an inert argon gas atmosphere). The potential was measured as the rest potential of the titanium plates which were of surface area $\sim 2\,cm^2$ and were referenced to determine the weight change of titanium metal in the molten salts. It was found that the mixed potential E, increased with the concentration of $TiCl_3$ in the molten salts and a steady state was obtained in about 30 min.

Fig. 3 shows the mixed potential versus time curves for titanium metal immersed in the KCl–NaCl molten salts with addition of K_2TiF_6. The measurement method was the same as that for titanium metal in KCl–NaCl molten salts containing $TiCl_3$ as mentioned above. It was also observed that the more titanium ions (Ti^{4+} or

Ti^{3+}) in the molten salts, the more positive the E value for the system (titanium metal/KCl–NaCl molten salts with $TiCl_3$ or K_2TiF_6). The potential is equal to $E_0 + (RT/nF)\,lna$ (where a is the activity of the titanium ions), if the (quasi) equilibrium of the reaction between the titanium plate and the molten salts is reached. The behaviour of the mixed potential versus time for titanium metal in the molten salts containing 0.276 mol % K_2TiF_6 was approximately similar to that for the system titanium/KCl–NaCl molten salts containing $TiCl_3$. This implies that the Ti^{4+} ions in the molten salts with 0.276 mol % K_2TiF_6 were reduced to Ti^{2+} ions in the same way as for the case of $TiCl_3$. However, the mixed potential for titanium metal in KCl–NaCl molten salts containing 1.37 mol % K_2TiF_6 initially increased rapidly, then decreased slowly and became stationary after about 30 min for the case of 1.37 mol % K_2TiF_6 and approximately 60 min for the case of 2.70 mol % K_2TiF_6.

The investigation of weight change of the titanium plate in KCl–NaCl molten salts containing $TiCl_3$ or K_2TiF_6 was carried out in order to
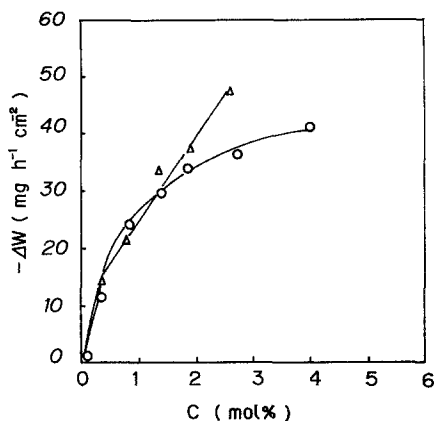
Fig. 4. Effects of the concentrations of titanium ions on weight change of titanium plate immersed in the molten salts containing K_2TiF_6 or $TiCl_3$ for 70 min at 973 K. $\bigcirc$, Ti^{4+}; $\triangle$, Ti^{3+}.

determine the relation between the weight change and the stationary mixed potential of titanium metal and to study the interaction between titanium and the molten salts. These results are given in Fig. 4, as plots of the weight change rate (the average rate in 70 min) of titanium metal versus the initial mol % of $TiCl_3$ or K_2TiF_6 in the molten salts. The rate of weight change increased approximately linearly in the case of $TiCl_3$, but non-linearly in the case of K_2TiF_6. The results are presented in Fig. 5 as plots of moles of $TiCl_3$ or K_2TiF_6 in the molten salts. The lines represent the theoretical weight change in accordance with various possible interaction mechanisms. From this figure the
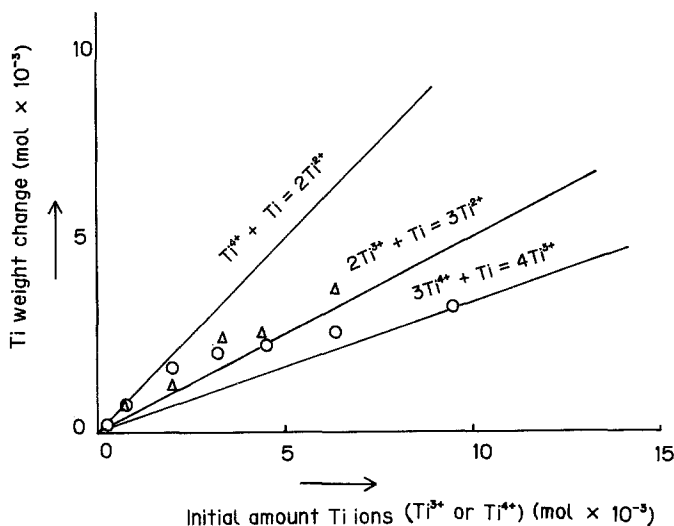
experimental results are in good agreement with the theoretical values for the interaction between titanium metal and the KCl–NaCl molten salts containing $TiCl_3$, which appears to follow the reaction $Ti + 2Ti^{3+} = 3Ti^{2+}$. But the interaction between titanium metal and the molten salt containing K_2TiF_6 is not simple. In the case of lower concentrations of K_2TiF_6 the experimental values agreed with the theoretical values of $Ti^{4+} + Ti = 2Ti^{2+}$. However, in the case of higher concentrations of K_2TiF_6 the experimental values appeared to agree with the theoretical values calculated according to $3Ti^{4+} + Ti = 4Ti^{3+}$.

3.2. X-ray diffraction analysis

From the results shown in Fig. 5, the mechanism of the interaction between titanium metal and the molten salts containing K_2TiF_6 appears complex, so it was necessary to determine the products of the interaction in order to clarify the reaction mechanism. Typical results of the X-ray diffraction analysis of insoluble materials through water leaching of the solidified salts are given in Fig. 6a–c. Besides the complex fluorides of trivalent titanium (K_2NaTiF_6, $KTiF_4$, $NaTiF_4$, K_3TiF_6, Na_3TiF_6), the lines for titanium metal were very strong in Fig. 6a, less strong in Fig. 6b and very weak in Fig. 6c. It is also noted that a few unclear lines in Fig. 6a and 6b exist.
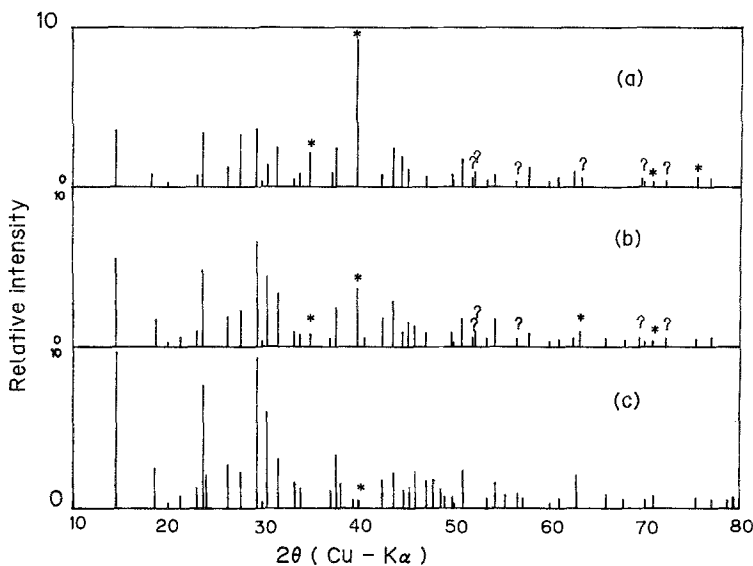

Fig. 5. Weight change of titanium plate dipped in the KCl–NaCl (15 g) molten salts containing various compositions of K_2TiF_6 ($\bigcirc$) or $TiCl_3$ ($\triangle$) at 973 K for 70 min. (The black lines represent theoretical weight change values with various possible reaction mechanisms.)

Fig. 6. X-ray diffraction of the products formed by the reaction between titanium metal and titanium ions in KCl–NaCl molten salts with various initial compositions of K_2TiF_6: (a) 0.276 mol %; (b) 1.370 mol %; (c) 3.994 mol %. In this figure the lines marked with an asterisk are those of metal titanium; the lines marked with a question mark are unclear lines; the other lines are those of trifluoride compounds of titanium ($KTiF_4$, K_2NaTiF_6, K_3TiF_6, $NaTiF_4$, Na_3TiF_6).

3.3. *Impedance measurements*

In order to elucidate the mechanism of the reaction between titanium metal and titanium ions in the molten salts, impedance measurements were carried out. Fig. 7 shows typical complex impedance diagrams for the interactions between titanium metal and the KCl–NaCl molten salts containing $TiCl_3$ or K_2TiF_6 at mixed potential. Fig. 7 gives results for the case of 0.276 mol % K_2TiF_6 or 1.37 mol % $TiCl_3$, but the other diagrams for the reaction with various compositions of $TiCl_3$ or K_2TiF_6 showed the same behaviour as those in Fig. 7. It is evident that the
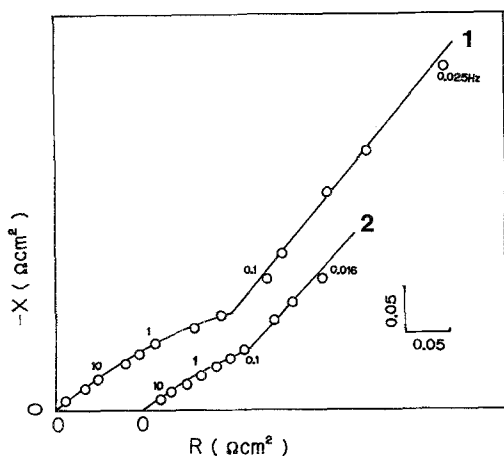

Fig. 7. Complex impedance diagrams of titanium metal at mixed potential in KCl–NaCl containing (1) K_2TiF_6 or (2) $TiCl_3$ at 973 K. 1, 0.276 mol %; 2, 1.370 mol %.

complex impedance diagrams consist of two parts for both $TiCl_3$ and K_2TiF_6: the loop on the higher frequency side is due to kinetically sluggish reactions, and the straight line with a slope of about 45° on the lower frequency side is attributed to diffusion of reactants or reaction products [21]. Thus, the reaction rate is controlled by slow kinetics and the diffusion of reactants or products. However, from the results shown in Fig. 7 alone, it can not be deduced which part of the interaction, the anodic part or the cathodic part, was the controlling step, so the following impedance measurements were performed. These results are shown in Figs 8 and 9. Fig. 8 shows the complex impedance diagrams for the cathodic reactions of $TiCl_3$ or K_2TiF_6 in the molten salts at potentials which were near the mixed potential shown in Fig. 2 and Fig. 3. Fig. 9 shows those for titanium metal in pure KCl–NaCl under anodic polarization at a potential which was also near the mixed potentials. The impedance diagrams for the reduction reactions appear to be straight lines with slopes of about 45° in the complex impedance diagram. This is characteristic of a diffusion-controlled reaction. However, the impedance diagrams for the anodic reaction of titanium metal in pure KCl–NaCl molten salts contained not only a kinetically sluggish anodic reaction part but also a diffusion part due to titanium ion transfer.

The relation between the impedances at mixed potential and the weight changes of titanium
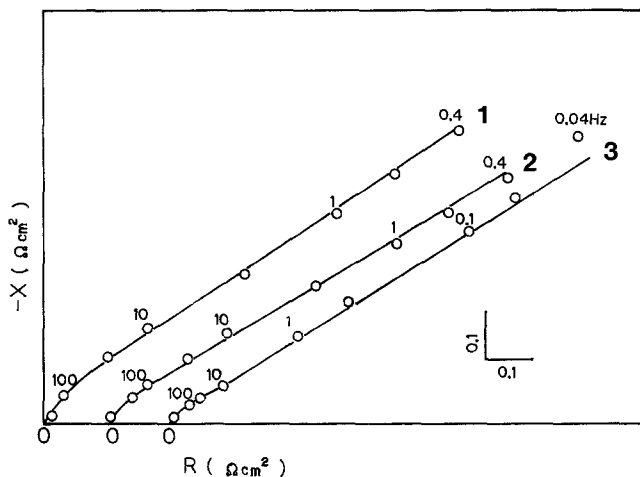
Fig. 8 Complex impedance diagrams of the reduction reaction of titanium ions on platinum electrode in the KCl–NaCl molten salts containing $TiCl_3$ or K_2TiF_6 at 973 K. 1, 1.37 mol % $TiCl_3$, $E = -1$ V; 2, 1.37 mol % K_2TiF_6, $E = -0.6$ V; 3, 1.37 mol % K_2TiF_6, $E = -0.9$ V.

metal immersed in KCl–NaCl molten salts containing various compositions of $TiCl_3$ or K_2TiF_6 was also obtained. As a first approximation the reaction resistance was taken as the difference, Rf^*, of the real component between the inflexion point of the curve of the complex impedance diagrams and the highest frequency. These results are given in Fig. 10 as plots of $1/Rf^*$ versus the average weight change rates (ΔW mg hr^{-1} cm^{-2}). There was a straight line relation for titanium metal in the molten salts with $TiCl_3$, but in the case of K_2TiF_6 a straight line relation was not observed. The implication is that the mechanism of the reaction between titanium metal and the molten salts containing K_2TiF_6 changed with the K_2TiF_6 content.

4. Discussion

In Fig. 5 it was shown that the weight change of titanium metal in the molten KCl–NaCl–$TiCl_3$ agreed well with the theoretical values calculated as the following reaction.

$$2Ti^3 \text{ (complex)} + Ti \text{ (s)} = 3Ti^{2+} \text{ (complex)} \tag{1}$$
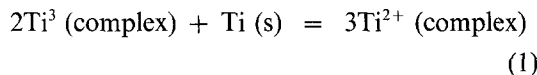
From the results in Figs 4, 5 and 10, the interaction between titanium metal and the molten KCl–NaCl–K_2TiF_6 was different from the reaction between titanium metal and the molten KCl–NaCl–$TiCl_3$. When the composition of K_2TiF_6 was higher than 2.76 mol % (about 9.1 wt %), the weight change of the titanium specimen agreed well with the theoretical
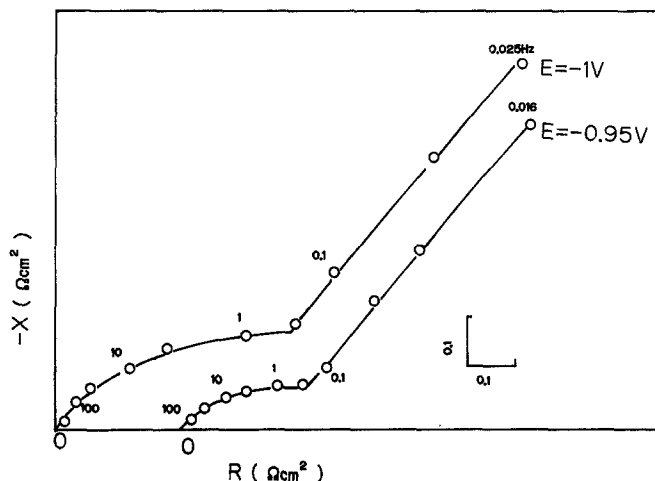

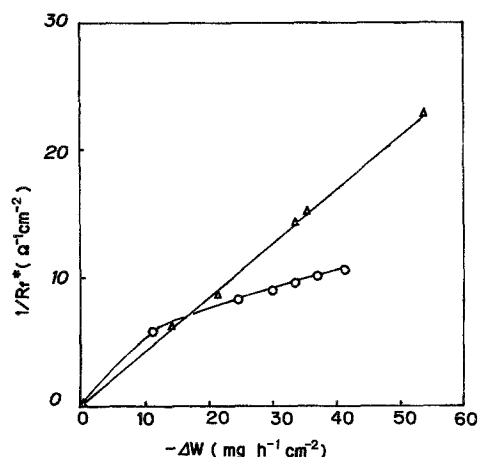Fig. 9. Complex impedance diagrams of titanium metal at anodic polarization in the KCl–NaCl molten salts at 973 K.

Fig. 10. Relations between rate of weight change (the average rate of 70 min) of titanium plate and $1/Rf^*$ (where Rf^* is the difference of the real component between inflexion point of the curves of complex impedance diagrams of titanium plate at mixed potential) and the highest frequency in the KCl–NaCl molten salts with $TiCl_3$ (△) or K_2TiF_6 (○) at 973 K.

values calculated as the reaction $3Ti^{4+} + Ti = 4Ti^{3+}$, where the products were determined as titanium trifluoride group in Fig. 6c. These results were consistent with those obtained by many researchers [17, 18, 22, 23]. Therefore, the interaction between titanium metal and the molten salts with a K_2TiF_6 content higher than about 9 wt % can be indicated as

$$3Ti^{4+} + Ti = 4Ti^{3+} \qquad (2)$$
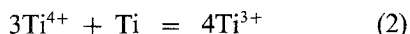
When the concentration of K_2TiF_6 was less than approximately 0.8 mol %, the experimental results were in close agreement with the theoretical values calculated by the reaction $Ti^{4+} + Ti = 2Ti^{2+}$. However, only titanium trifluoride compounds and titanium metal in the products were detected according to X-ray diffraction analysis results. This may be because of the decomposition of Ti^{2+} (fluoride) during cooling [24, 25]. Then the reaction of titanium metal in the molten salts with a K_2TiF_6 content of less than about 0.8 mol % proceeded as follows:

$$Ti^{4+} + Ti = 2Ti^{2+} \text{ (fluoride or chloride)} \quad (3)$$
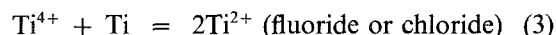
From the results in Figs 5 and 6, the interaction between titanium metal and the molten salts containing K_2TiF_6 with compositions between 0.8 and 2.7 mol % was represented by Reactions 2 and 3.

According to the impedance measurement results, Reactions 1, 2 and 3 were controlled by charge transfer and diffusion.

From the results in the literature [26, 27], the relation between Rf^* and ΔW is as follows:

$$1/Rf^* = K[\alpha_a n_a + (1 - \alpha_c)n_c]n_{app}\Delta W \qquad (4)$$

where K is a constant at constant temperature, n_{app} is the apparent electron number, n_a is the anodic electron number, n_c is the cathodic electron number, and α_a and α_c are the transfer coefficients of the anodic and cathodic reactions of the interaction reactions between titanium metal and the molten salts. Because the reaction does not vary with the composition in the case of $TiCl_3$, $[\alpha_a n_a + (1 - \alpha_c)n_c]$ is almost constant. There exists a simple relation between $1/Rf^*$ and ΔW. As the reaction between titanium metal and the molten $KCl–NaCl–K_2TiF_6$ changes with the composition, $[\alpha_a n_a + (1 - \alpha_c)n_c]n_{app}$ may change (Fig. 10).

The electroreduction reaction of Ti^{4+} ions in chloride molten salts [1, 6, 28, 29] proceeds according to

$$Ti^{4+} + e = Ti^{3+}$$
$$Ti^{3+} + e = Ti^{2+}$$
$$Ti^{2+} + 2e = Ti$$
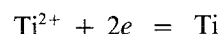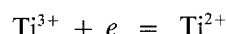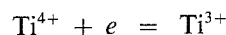
in fluoride–chloride or fluoride molten salts, the reduction reactions are [17, 18, 22]:

$$Ti^{4+} + e = Ti^{3+}$$
$$Ti^{3+} + 3e = Ti$$
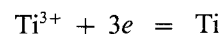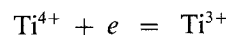
However, from the results in this experiment, if the composition of K_2TiF_6 was less than 0.8 mol %, the reaction, $Ti^{4+} + Ti = 2Ti^{2+}$, occurred. It can be concluded that, if the concentration of K_2TiF_6 is less than 0.8 mol %, the behavior of Ti^{4+} ions acts like chloride titanium ions in KCl–NaCl or LiCl–KCl molten salts.

It can also be reasonably assumed that the complex titanium ions were changing from $TiF_x^{(x-4)-}$ into $TiF_xCl_y^{(x+y-4)-}$ or $TiCl_y^{(y-4)-}$ with decrease of the concentration of K_2TiF_6 in the KCl–NaCl molten salts. Therefore, the behaviour of titanium ions with less than 0.8 mol % K_2TiF_6 content is very similar to that in the molten salts with $TiCl_3$.

5. Conclusion

Based on the experimental data obtained by use of a.c. impedance measurements, mixed potential measurements, weight change measurements and X-ray diffraction, a different mechanism is proposed for the reaction between titanium and titanium ions in molten salts containing $TiCl_3$ or K_2TiF_6, respectively. In the case of $TiCl_3$ the reaction can be considered to proceed according to $2Ti^{3+} + Ti = 3Ti^{2+}$. However, in the case of K_2TiF_6 it is more complex. If the concentration of K_2TiF_6 is higher than 2.7 mol %, the reaction can be concluded to be $3Ti^{4+} + Ti = 4Ti^{3+}$. If the concentration is less than 0.8 mol %, the reaction is $Ti^{4+} + Ti = 2Ti^{2+}$ and $3Ti^{2+} = Ti + 2Ti^{3+}$ (during cooling). These reactions are controlled by charge transfer and diffusion simultaneously.

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