Preparation of Titanium from TiCl_4 in a Molten Fluoride-chloride Salt

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ABSTRACT

Titanium was prepared from TiCl_4 in molten NaCl-KCl-NaF salt. The product of the reaction of TiCl_4 with NaF was identified using X-ray diffraction, and its electrochemical behavior was studied using cyclic voltammetry and square wave voltammetry. The electrochemical deposition of titanium was investigated during the addition of TiCl_4 to NaCl-KCl-NaF melts. The results indicate that Na_2TiF_6 was first obtained through the reaction of NaF with TiCl_4 in the NaF-KCl-NaCl melt, and Na_2TiF_6 was decomposed to Na^+ and $[\text{TiF}_6]^{2-}$ in the melts. $[\text{TiF}_6]^{2-}$ was then sequentially reduced to $[\text{TiF}_6]^{3-}$ and Ti at the cathode, accompanied by chlorine gas emission at the anode and fluoride formation at the cathode.

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1. Introduction

Currently, the Kroll process is used for the industrial to production of metallic titanium. This process consists of three steps, which include: the conversion of TiO_2 to TiCl_4 , the subsequent reduction of TiCl_4 to titanium by liquid Mg , and the electrolysis of the MgCl_2 byproduct. However, the process is expensive because reduction and distillation require a long time, production is intermittent, and consumes large amounts of energy during the electrolysis step. A simpler and more compact single-step would be desirable for the direct conversion of TiO_2 or TiCl_4 into titanium in order to achieve high productivity at low energy costs.^{1,2}

The direct electrolysis of TiO_2 , which is a novel method of electro-deoxidization, was first realized in the FFC Cambridge process in 2000.³ In this oxide electrolysis process, the semiconductor TiO_2 acts as the cathode and is reduced in a CaCl_2 electrolyte. As the TiO_2 is slowly consumed, solid titanium is produced, and the resulting oxygen diffuses from the cathode into the melt. Unfortunately, very long electrolysis times are required to achieve significant conversions, and current efficiencies are low. Furthermore, production remains restricted to batch processes.^{4,5} Another method of preparing titanium metal from TiO_2 involves the consumption of the anode during electrolysis. In this process, an electronically conductive material is produced through carbothermal reduction of TiO_2 , which is then used as the anode in an NaCl-KCl-TiCl_x ($2 \leq x \leq 3$) electrolyte. During electrolysis, low-valence titanium ions dissolve into the melt and are deposited as titanium at the cathode.^{6–10} Efficiency and product quality are significantly increased in this process compared to those of the FFC process; however further studies are required for the large-scale preparation of anode materials and industrial scale-up.

Since the 1980s, the Marco Ginatta Company has studied the direct industrial production of titanium from TiCl_4 .¹¹ Unfortunately, this project was ultimately abandoned because of an inability to control production costs. Since then, Wurm et al. obtained titanium deposits via electrolysis in a molten chloride-fluoride mixture.¹² However, this process faced problem of the low current efficiency and poor-bath stability.

It is well known that ions complexes, such as $[\text{TiF}_6]^{2-}$, are formed by low valence titanium cations and fluoride anions in NaCl-KCl-NaF melts, and those complexes can be reduced to form titanium metal at the cathode.^{13,14} This implies that $[\text{TiF}_6]^{2-}$ is obtained through the reaction TiCl_4 with fluoride salt. Therefore, this study presented a direct electrolysis process for producing titanium from TiCl_4 in molten NaCl-KCl-NaF . The reaction mechanism of TiCl_4 and fluoride salts and the electrochemical behaviors of titanium ions were discussed. Furthermore, the electrolytic preparation of titanium was studied under continuous addition of TiCl_4 .

2. Experiment

2.1 Preparation of the fluoride-chloride salt

A previous investigation revealed that the NaCl-KCl-NaF system has a minimum point at the temperature of 879 K and a composition of NaCl (41.75 mol%)– KCl (41.75 mol%)– NaF (16.5 mol%).¹⁵ Therefore, the electrolyte used in these experiments consisted of an equimolar of NaCl-KCl melt containing 20 mol% NaF (reagent grade, Beijing Chemical Industries, Beijing, China) and all of the electrochemical experiments were conducted at 1023 K. The salt was dried under vacuum for at least 6 h at 673 K to remove the moisture before heating to 1023 K under argon atmosphere. After melting the salt, the dried hydrogen chloride ($\text{HCl} \geq 99.9\%$, Chengdu Heng Yuan Co., Ltd., Chengdu, China) was bubbled into the melt for 1 h to remove oxide ions and water. Argon was then used for the melt for 40 min to remove all dissolved hydrogen chloride from the salt.¹⁶

After the system reached a pre-set temperature, TiCl_4 (reagent grade, Beijing Chemical Industries, Beijing, China) gas was slowly charged into the bath, and samples were removed from the salt with a quartz tube at different mole fractions of TiCl_4 . The concentration of fluoride and titanium ions in the sample were determined via titration¹⁷ and an inductively coupled plasma atomic emission spectrometer (ICP-AES; NexION 300D; PerkinElmer, USA),¹⁸ respectively, and the phase composition was measured via X-ray diffraction (XRD; X'pert PRO; PANalytical, Almelo, Netherlands).

Figure 1. (Color online) Schematic diagram of the electrochemical test system. 1-Ar outlet, 2-working electrode, 3-reference electrode, 4-counter electrode, 5-thermocouple, 6-Ar intake, 7-outer crucible, 8-inner crucible, 9-molten salt, 10-heating furnace.

Figure 3. (Color online) Relationship between the TiCl₄ mole fraction and $[F]/[Ti]$ at 1023 K.

Figure 2. (Color online) Schematic diagram of the experimental setup. 1-heating furnace, 2-circular hole, 3-graphite anode, 4-ceramic tube, 5-Ar outlet, 6-tail gas, 7-TiCl₄ inlet, 8-thermocouple, 9-Ar inlet, 10-carbon steel cathode, 11-outer crucible, 12-molten salt, 13-inner crucible.

2.2 Electrochemical experiments

A three-electrode setup, as shown in Fig. 1, was used to investigate the electrochemical behavior of the reaction product. A Mo wire (1 mm in diameter) sealed with a corundum tube was used as the working electrode. A pure graphite rod (2 mm in diameter) was used as counter electrode. An Ag/AgCl unit composed of a silver wire (1 mm in diameter) dipped into an alumina tube containing a silver chloride solution in an equimolar of NaCl-KCl (0.45 mol L^{-1}) was used as reference electrode.¹⁹ Cyclic voltammetry (CV) and other transient electrochemical techniques were performed using an electrochemical workstation (CHI860D; Beijing Chinese Science Days Co., Ltd., Beijing, China).

Titanium electrodeposits were prepared in the NaCl-KCl-NaF melt under continuous addition of TiCl₄ (0.4 mL min^{-1}). The anodic device was composed of a graphite plate ($500 \text{ mm} \times 25 \text{ mm} \times 3 \text{ mm}$) dipped into a ceramic tube. A carbon steel rod (20 mm in diameter) was used as cathode. The experimental setup is depicted in Fig. 2. Electrolysis was performed with a DC power (DPLP200; Shenzhen Kikusui Royal Ltd., Shenzhen, China) and the anode exhaust gas was absorbed via NaOH solution (0.25 mol L^{-1}). During electrolysis, the concentrations of chloride and fluoride ions in NaOH were determined by titration and titanium ions in the melt by ICP-

AES. After electrolysis, the electrodes were removed from the bath and washed in an ultrasonic tank containing a solution of water to remove all residual salt. Deposited products were subsequently dried and characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM; JSM-5600LV; JEOL Ltd., Tokyo, Japan).

3. Results and Discussion

3.1 Reaction mechanism of TiCl₄ in the NaCl-KCl-NaF melt

Figure 3 shows the changes in ratios of fluoride to titanium ions ($[F]/[Ti]$) after addition of TiCl₄ to the NaCl-KCl-NaF melt. $[F]/[Ti]$ decreased with increasing TiCl₄ content, following a trend that was consistent with theory when the TiCl₄ mole fractions below 3.33%. However, titanium and chloride ions were detected in the tail gas system, causing deviation between the experimental data and the theoretically expected values when the TiCl₄ mole fractions were above 3.33%. These results indicate that the TiCl₄ gas was fully dissolved in the melt with 20 mol% NaF at a TiCl₄ mole fraction below 3.33%.

Figure 4 shows the XRD patterns of the reaction products when different TiCl₄ mole fractions were used. The patterns shown in Fig. 4(a) indicated that no new phases formed without TiCl₄

Figure 4. (Color online) XRD patterns of the reaction products at different TiCl_4 mole fractions of (a) 0 mol%, (b) 2 mol%, and (c) 4.5 mol%.

addition. This was because the Gibbs free energy (ΔG^θ) of Reaction (1) was positive, indicating that NaF was more stable than KF in the melt.

As shown in Fig. 4(b), the product predominantly consisted of NaCl, KCl and NaF, with a large quantity of Na_2TiF_6 at 2 mol% TiCl_4 . This result indicated that TiCl_4 reacted with the NaCl-KCl-NaF melt to form Na_2TiF_6 at 1023 K. When the TiCl_4 concentration was increased to 4.5 mol%, peaks associated with NaF disappeared and the product mainly contained Na_2TiF_6 , NaCl, KCl, and a new K_2TiCl_6 phase (Fig. 4(c)). These results suggest that K_2TiCl_6 was formed as NaF was consumed. This likely occurred via the reaction of TiCl_4 with KCl to form K_2TiCl_6 as has been previously reported.^{20,21}

Multiple studies suggested that titanium ions can form a variety of complexes with anions in molten salts through complexation reactions, and the binding force of fluoride with titanium is higher than that of chloride with titanium.²² Therefore, NaF likely reacted with TiCl_4 to form Na_2TiF_6 and Na_2TiF_6 was decomposed to Na^+ and $[\text{TiF}_6]^{2-}$ in the melts.

It is difficult to determine Gibbs free energy in Eq. (3) due to a lack of Na_2TiF_6 thermodynamic data. However, the Gibbs free energy of Eq. (4) is below zero at 1023 K. Meanwhile, NaF is more stable than KF in the melt shown in reaction (1). In combination, these observations suggest that the reaction product of TiCl_4 and NaF was primarily Na_2TiF_6 in the NaF-KCl-NaCl melt.

Figure 5. (Color online) Cyclic voltammogram in the NaCl-KCl-NaF melt with a scan rate of 100 mV s^{-1} (a) and after TiCl_4 addition at different scan rates (b) at 1023 K.

3.2 Electrochemical behavior of $[\text{TiF}_6]^{2-}$

Figure 5(a) shows a typical cyclic voltammogram in the NaCl-KCl-NaF electrolyte system. The curve exhibits a large and sharp redox couple (A/A') at approximately -1.7 V , corresponding to the deposition and dissolution of sodium metal.²³ Except for this redox couple, no other obvious electrochemical signals could be observed in Fig. 5(a). However, two pairs of redox couples (B/B' and C/C') were observed with two cathodic peaks at -0.64 and -0.07 V after 2 mol% TiCl_4 was added into the melt (Fig. 5(b)). Positions of redox couples remained essentially unchanged with increasing scanning rate. These results suggest that the reduction of Na_2TiF_6 proceeded via two steps and that the redox system was quasi-reversible.

To further characterize both reduction peaks, square wave voltammetry was performed under testing parameters of 50 mV pulse height and 10 Hz frequency in the NaCl-KCl-NaF- TiCl_4 (2 mol%) at 1023 K. Figure 6 shows SWV curve, exhibiting two peaks (B and C) in the potential range -0.9 to 0.4 V and their positions corresponded with the CV results shown in Fig. 5. However, a sharp, incomplete, bell-shaped, and symmetrical signal was clearly observed at a potential of -0.65 V (B). The disturbance of the signal could be attributed to a nucleation effect and could only be resolved by considering the decreasing part of the peak when measuring the half peak width.²³ Therefore, each reduction peak was fitted to a Gaussian curve, and the relationship between the width at half peak maximum ($W_{1/2}$) and the numbers of electrons exchanged (n) followed the following equation at low frequency values.²⁴

$$W_{1/2} = 3.52 \frac{RT}{nF} \quad (5)$$

Where $W_{1/2}$ is the width of the half peak, n is the number of the exchanged electrons, T is the temperature, F is the Faraday constant, and R is the ideal gas constant.

The calculated values of n for peaks B and C in Fig. 6 were 1.09 and 3.05, respectively. Wrum et al. reported that $[\text{TiF}_6]^{2-}$ and

Figure 6. (Color online) Square wave voltammogram in the NaCl-KCl-NaF-TiCl₄ (2 mol%) at 1023 K. Pulse height 50 mV; frequency 10 Hz.

Figure 8. (Color online) Current-time curve under the electrolytic potentiostatic value of -0.07 V vs. Ag/AgCl and -0.65 V vs. Ag/AgCl.

Figure 7. (Color online) XRD spectra of salt samples at the electrolytic potentiostatic value of (a) -0.07 V vs. Ag/AgCl and (b) -0.65 V vs. Ag/AgCl.

$[\text{TiF}_6]^{3-}$ are the stable species in NaCl-KCl-NaF eutectic melts, and that two electron transfer steps existed in the reaction under the experimental conditions.¹² The authors suggested that the two-step reduction of $[\text{TiF}_6]^{2-}$ likely proceeded by Reactions (6) and (7). According to the research by Song et al., it has been calculated that the theoretical redox potential of Eqs. (6) and (7) were -0.12 and -0.46 V, respectively.²² This may well explain why the potential of Eq. (6) was lower than that of Eq. (7).

Based on the results of CV and SWV, potentiostatic electrolysis was conducted at -0.07 V vs. Ag/AgCl and -0.65 V vs. Ag/AgCl for 2 h in NaCl-KCl-NaF-TiCl₄ (3 mol%) melts. After electrolysis, samples were removed from the melts, using a quartz tube and measured via XRD spectra.

Figure 7 shows the XRD patterns of the salt samples at the electrolytic potentiostatic values of -0.07 and -0.65 V. The results showed that the Na₃TiF₆ phase was formed at -0.07 V; however, it was not found at -0.65 V, which was consistent with the SWV results.

The relationship between time and current is presented in Fig. 8. Showing that the current density value at -0.65 V was bigger than -0.07 V and the current density value gradually increased with ongoing electrolysis. This phenomenon may be the result of growth

Figure 9. (Color online) Cell voltage-time curve during electrolysis (a), chloride mole fraction in the NaOH solution (b), and mole fraction of titanium ions in the melt (c).

of the crystals. Therefore, to obtain titanium at the cathode, the current density of reducing Na₂TiF₆ to Ti was no less than 0.25 A cm^{-2} .

3.3 Electrochemical deposition

Electrochemical deposition was conducted under a constant current at 1023 K, and the cathodic and anodic current densities were 0.30 and 0.5 A cm^{-2} , respectively. Prior to electrolysis, TiCl₄ (1 mol%) was injected into NaCl-KCl-NaF eutectic melts at 0.4 mL min^{-1} . To further understand the process of electrolysis, the compositions of the vent gas and the titanium ion concentration in the melt were measured via titration.

The value of cell voltages (E) and the concentrations of titanium ions ($C_{[\text{Ti}]}$) in the molten salt and of chloride ions ($C_{[\text{Cl}]}$) in the NaOH solution during electrolysis are shown in Fig. 9. Figure 9(a) shows that the cell voltage rapidly increased during the first three

Figure 10. (Color online) XRD pattern (a) and SEM image (b) of the electrochemically deposited product.

Table 1. Comparison of the chemical composition of titanium metal under different process experimental conditions (in wt%).

Ti	N	C	H	O	Cl	Fe	Si	Mn	Mg	Ref.
99.3	0.11	0.1	—	0.27	—	0.168	0.02	—	0.01	27
—	0.01	0.3	—	0.2–0.6	—	trace	—	trace	—	28
—	0.03–0.05	0.05	0.02	0.2–0.4	0.2–0.4	0.05	—	—	—	29
99	0.04	0.008	0.029	0.42	0.05	0.011	0.02	0.018	0.01	This work

Table 2. Comparison of the cathodic current efficiency under different process experimental conditions.

Raw material	Bath composition	T (K)	J (A cm ⁻²)	η (%)	Ref.
Na ₂ TiF ₆ /K ₂ TiF ₆	NaCl-KCl	953–983	5–10	41.3–48.5	12
K ₃ TiF ₆	LiF-NaF-KF	1023	0.05–0.075	60–65	27
TiCl ₄	NaCl-KCl-LiCl-TiCl ₂ -TiCl ₃	1623	0.5	27.5	28
TiCl ₄	NaCl-KCl	998	0.09–0.37	20–90	30
TiCl ₄	NaCl-KCl-NaF	1023	0.3	63.1–66.7	This work

minutes due to the influence of potentiodynamic polarization, and then the cell voltage gradually decreased due to the growth of the cathodic product.

Chloride ions were not detected prior to electrolysis, while a large amount of chloride ions were found in the NaOH solution during electrolysis (Fig. 9(b)); however fluoride ions were not detected throughout the entire electrolysis process. These results indicate that the anodic oxidation reactions converted chloride ions to chlorine gas at the anode, while fluoride ions remained in the melts.²⁵

Prior to electrolysis, the concentration of titanium ions in melts increased linearly with TiCl₄ addition; however this trend eased during the electrolysis (shown in Fig. 9(c)). This phenomenon might be caused by the reduction of titanium ions to titanium metal at the cathode.

The XRD patterns of an electrochemically deposited product are shown in Fig. 10(a). Pure titanium metal was obtained at the cathode. Impurities content of the cathodic product was measured and the results were shown in Table 1. The results suggested that the chemical compositions of titanium in this study are close to the previous research. A SEM image of the deposited product is shown in Fig. 10(b). The metallic titanium had granular structures with diameters of ~1 to 10 μm and rod-shaped structures with sizes of ~1 to 2 μm (diameter) by ~20 to 50 μm (length). These different structures might have resulted from the disproportionation reaction of [TiF₆]³⁻.²⁶

Titanium metal can be prepared from TiCl₄ in the NaCl-KCl-NaF melt through Reactions (2), (8), and (9) combined.

The cathodic current efficiency of electrochemical deposit was calculated via Eq. (12).

$$\eta = \frac{m}{0.448it} \quad (12)$$

Where η is current efficiency, m is the mass of titanium, i is the current intensity, and t is the electrolysis times.

Table 2 shows titanium prepared from TiCl₄, K₂TiF₆ or Na₂TiF₆ under different experimental conditions. The current efficiency value obtained in this work (63.1%–66.7%) was superior to the preparation of titanium from K₂TiF₆ or Na₂TiF₆ and was in the middle of TiCl₄ direct reduction. This phenomenon could be attributed to the instability of the salt bath and influence of the diaphragm in previous studies.²⁹ According to Eq. (12), the loss of the current efficiency may be caused by the loss of titanium metal, which was affected by the titanium powder particle and the cyclic oxidation-reduction of [TiF₆]³⁻ between the anodic and cathodic area.³¹

4. Conclusions

Titanium metal was prepared via the electrochemical reduction of TiCl₄ in NaCl-KCl-NaF eutectic melts. Major results can be concluded as follows:

(1) Na_2TiF_6 was obtained via TiCl_4 reaction with NaF in NaCl-KCl-NaF melts at 1023 K, and was decomposed to Na^+ and $[\text{TiF}_6]^{2-}$ in the melts.

(2) The reduction process of hexafluorotitanate ions was $[\text{TiF}_6]^{2-}$ to $[\text{TiF}_6]^{3-}$ and then to Ti at the cathode. The reduction degree of $[\text{TiF}_6]^{2-}$ was affected by the electrolytic potentiostatic value.

(3) Pure titanium and chloride gas were obtained under a constant current at the cathode and anode, respectively. The current efficiency in this work reached 63.1%–66.7%.

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