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Effect of fluoride ions on coordination structure of titanium in molten NaCl–KCl

Shanshan Liu^{1,2}, Shaolong Li^{1,2}, Chenhui Liu², Jilin He^{1,2}, and Jianxun Song^{1,2},✉

1) Henan Province Industrial Technology Research Institute of Resources and Materials, Zhengzhou University, Zhengzhou 450001, China

2) School of Material Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

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Abstract: The effects of fluoride ions (F^-) on the electrochemical behavior and coordination properties of titanium ions (Ti^{n+}) were studied in this work, by combining electrochemical and mathematical analysis as well as spectral techniques. The α was taken as a factor to indicate the molar concentration ratio of F^- and Ti^{n+} . Cyclic voltammetry (CV), square wave voltammetry (SWV), and open circuit potential method (OCP) were used to study the electrochemical behavior of titanium ions under conditions of various α , and *in-situ* sampler was used to prepare molten salt samples when α equal to 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 8.0. And then, samples were analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The results showed that F^- in molten salt can reduce the reduction steps of titanium ions and greatly affects the proportion of valence titanium ions which making the high-valence titanium content increased and more stable. Ti^{2+} cannot be detected in the molten salt when α is higher than 3.0 and finally transferred to titanium ions with higher valence state. Investigation revealed that the mechanism behind those phenomenon is the coordination compounds ($TiCl_nF_i^{m-}$) forming.

Keywords: molten salt; sodium chloride–potassium chloride; ratio of fluoride and titanium ions; coordination mechanism

1. Introduction

High purity titanium has excellent properties, such as light weight, high corrosion resistance, high melting point, low resistivity [1–3]. It is mainly used in large-scale integrated circuit manufacturing of high-end new titanium alloy and other industries [4–6]. It is a necessary strategic critical material for electrical and electronics, and aerospace. Among many preparation technologies of high purity titanium, molten salt electrolysis, as a simple process and easy to realize continuous process, has a very broad application prospect and attracts much attention. Considering the electro-refining process, firstly, it is necessary to prepare molten salt containing low valence titanium ions which uses $TiCl_4$ and high purity titanium [7], which is used as titanium ion source to add eutectic salt in electro-refining cell. Secondly, sponge titanium (95wt%–99wt%) is taken as anode and high purity titanium plate as cathode, and then the electrochemical dissolution of titanium and electrochemical deposition of high purity titanium occur at anode and at cathode, respectively. Finally, high purity titanium products with different morphology and quality are obtained under various electrolysis parameters.

Due to sundry oxidation states of titanium ions, the process of electrolytic production of titanium was complex and involves multi-step process, resulting in low current efficiency [8–11]. There were mainly three possible valence states of titanium ion in chloride melt, namely Ti^{2+} , Ti^{3+} , and

Ti^{4+} . It has been demonstrated by several researchers that equilibriums exist between metallic titanium and three ions states (Ti^{2+} , Ti^{3+} , and Ti^{4+}) [11–15]:



The element of electrolyte has an important effect on the equilibrium of titanium ions in molten salt and the electrodeposition process of titanium. All kinds of molten salt electrolytes including chlorine, fluoride, and chloro-fluoride have been studied in detail [16–17]. In molten chlorides, the reduction of Ti(IV) follows the steps of $Ti(IV) \rightarrow Ti(III)$, $Ti(III) \rightarrow Ti(II)$, and $Ti(II) \rightarrow Ti$. However, there are some differences in electrochemical behavior in various chloride systems [18–20]. In the fluoride based molten salt, there is usually no intermediate reduction step involving Ti(II) ions. It means that the presence of fluoride causes Ti(III) to stabilize in the form of TiF_6^{3-} . Ti(III) is supposed to be reduced directly to the metal when the concentration of fluoride is high enough, and it will also involve an intermediate reduction step with a lower fluoride concentration [21–24]. In full-fluoride melts, the deposition of titanium may occur directly from trivalent species, and a two-step reduction for Ti(IV) to titanium metal: $Ti(IV) \rightarrow Ti(III)$ and $Ti(III) \rightarrow Ti$ [25].

Titanium free ions exist in Ti^{2+} , Ti^{3+} , and Ti^{4+} states in different molten salts, specifically, in anodic dissolution, and anions such as Cl^- or F^- will combined with the dissolved

✉ Corresponding author: Jianxun Song E-mail: songjx00@163.com

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high-valence titanium ions to form a stable coordination compounds, which made the high-valence titanium ions exist stably, so as to affect the existence of different valence titanium ions in the molten salt.

It has been studied that titanium ions exist in form of complexes in molten chloride salts, TiCl_i^{m-} . When a certain amount of fluoride ion is added to the electrolyte, titanium ions in intermediate valence states will undergo disproportionation reactions as shown in reactions (1) and (2), and the equilibrium of the reaction will be broken down. Fluoride ion has a smaller ionic radius compared with chloride, and it was more likely to form coordination relationship with cation in molten salt [26–30].

Therefore, titanium ions and fluoride ions will form coordination compounds: TiF_i^{m-} . The formation of these compounds changes the equilibrium of above disproportionation reactions. However, the specific forms and reaction mechanisms of these coordination compounds is not clear. In this research, we introduced fluoride ions into NaCl–KCl molten salts to in-depth study of the coordination mechanism of Ti–F ions. It is of great significance for revealing the mechanism of reduction process and electrolytes selecting.

2. Experimental

2.1. Preparation of titanium ions

In our previous work [7], TiCl_3 was obtained by the reaction of TiCl_4 (TiCl_4 , Sinopharm Chemical Reagent Co., Ltd., analytical grade 99.0wt%) with titanium metal in the CaCl_2 (CaCl_2 , Sinopharm Chemical Reagent Co., Ltd. Analytical grade 99.99wt%) melt. In this research, titanium ions were synthesized by the reaction of TiCl_4 (TiCl_4 , $\geq 99.9\text{wt}\%$ purity) with sponge titanium in the NaCl–KCl melt, and the molar ratio of Ti and TiCl_4 ($n_{\text{Ti}} : n_{\text{TiCl}_4}$) was equal to 1:4. NaCl and KCl (NaCl, $\geq 99.5\text{wt}\%$ purity; KCl, $\geq 99.5\text{wt}\%$ purity; mass ratio of 0.44:0.56) were applied as electrolyte with the weight of 1000 g. It was first pre-melted at 1023 K, and then, titanium sponge was placed into the pre-melted salt, and the temperature was re-heated to 1023 K under the protection of high-purity argon atmosphere (99.999wt%) for 4 h. The resistance furnace was vacuumed, and the TiCl_4 liquid was

slowly injected into the reactor under slight negative pressure. The flow rate of TiCl_4 was controlled by valve to regulate the reaction rate so that TiCl_4 could react fully with titanium sponge in the reactor. After all the TiCl_4 was injected, it was kept for 6–8 h and lowered to room temperature under the protection of argon gas. Finally, the salt was taken out and stored in a glove box for later use.

2.2. Electrodes and electrochemical techniques

Low-valence state titanium was measured by cyclic voltammetry (CV), square wave voltammetry (SWV), and open circuit potential method (OCP) tests in a three-electrode system, a glassy carbon (3.0 mm in diameter) was used as the working electrode, and a platinum wire (2.0 mm in diameter) and a graphite rod (5.0 mm in diameter) were used as reference electrode and counter electrode, respectively. In order to be more comparable, the reference potential was converted to Cl_2/Cl^- . When determining the anodic polarization curve, a glassy carbon (2.0 mm in diameter), a graphite rod (5.0 mm in diameter), and a nickel wire (1.0 mm in diameter) were used as working electrode, counter electrode, and reference electrode, respectively. All of potentials in the following experimental were calibrated to Cl_2/Cl^- .

2.3. Sample preparation and characterization

The concentrations of Ti^{2+} and Ti^{3+} were determined by dihydrometric method and ferric ammonium sulfate titration method, respectively. The total amount of titanium ion was determined by spectrophotometry. In this research, the total concentration of titanium ion was 15.41wt%, among them, $w_{\text{Ti}^{2+}} = 8.30\text{wt}\%$, $w_{\text{Ti}^{3+}} = 3.18\text{wt}\%$, and $w_{\text{Ti}^{4+}} = 3.93\text{wt}\%$, which was used as titanium ion source. Molten salt containing 10.0wt% titanium ions was obtained by dilution of titanium concentration, and KF (KF, $\geq 99\text{wt}\%$ purity) was used as the source of fluoride ions. Fig. 1 (a) shows the equipment diagram of *in-situ* online feeding feeder. The basic feeding process is to load KF at the top of the feeding tube and then substitute KF into the molten salt by means of argon flow. Then, a quartz rod (6.0 mm in diameter) was inserted into the melt under different concentrations of fluoride ions and was quickly pulled out to take a molten salt sample, which was re-

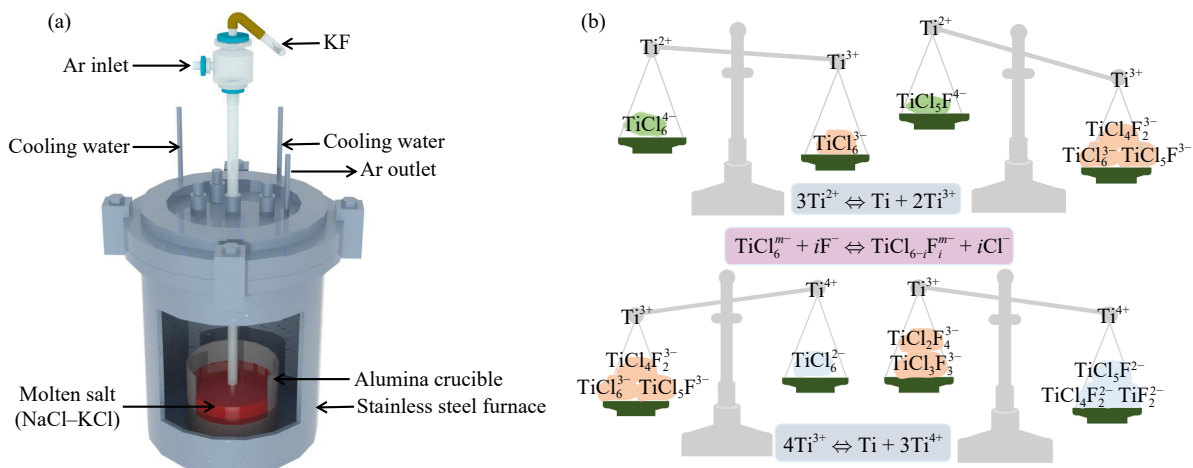


Fig. 1. (a) Equipment diagram of *in-situ* online feeding; (b) schematic diagram of equilibrium mechanism.

ported in detail in our previous work [31]. The attached melt was cooled to the solid state and collected.

The samples under different conditions, the molar concentration ratios of F^- and Ti^{n+} ($[F^-]/[Ti^{n+}]$, i.e. α) with 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 8.0, were obtained by adding fluoride ion according to above method. After adding of fluoride ions, titanium ions will react with them to give coordination compounds. In order to observe the possible type of the complexes, the molten salts with different amounts of fluoride ions were sampled and analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy.

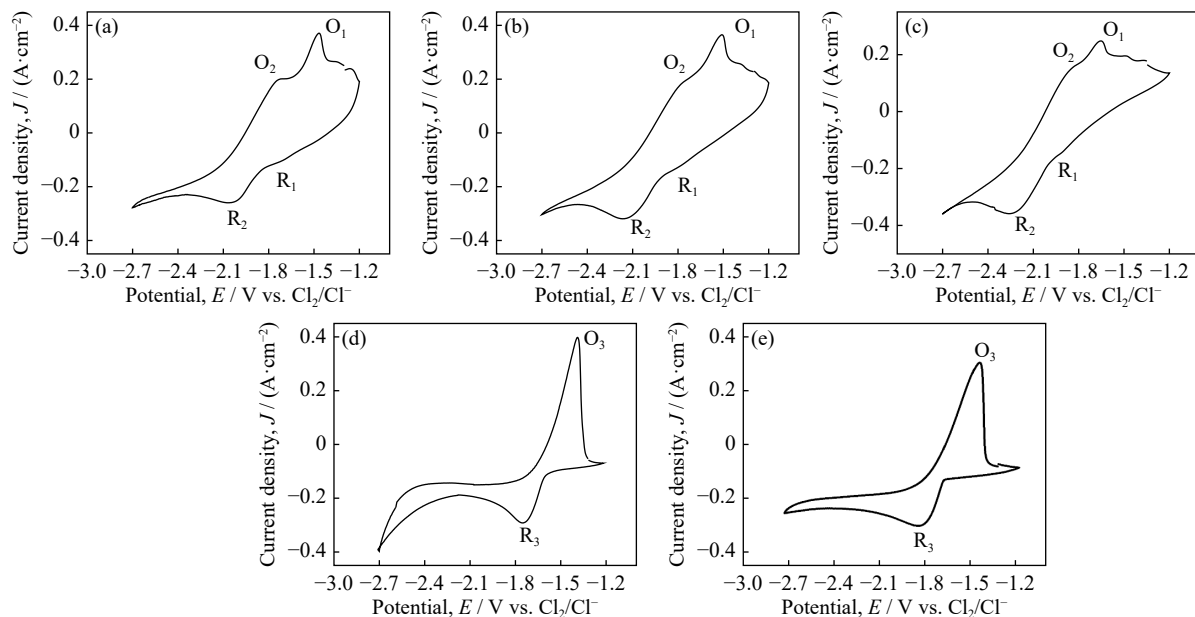


Fig. 2. Cyclic voltammogram of titanium ions in NaCl–KCl melt on the glassy carbon electrode at various α values: (a) $\alpha = 0$; (b) $\alpha = 1.0$; (c) $\alpha = 2.0$; (d) $\alpha = 3.0$; (e) $\alpha = 5.0$. Reference electrode (RE): Cl_2/Cl^- ; counter electrode (CE): graphite.

A more accurate SWV method was used for testing. as shown in Fig. 3, it can be seen that the reduction steps and reduction potential correspond to CV results. The number of exchanged electrons associated with reducing peaks, R_1 , R_2 , and R_3 , were measured by SWV.

The relationship between the peak half width ($W_{1/2}$) and the number of exchanged electrons involved in the reaction (n) can be expressed as Eq. (3) [32–33]:

$$W_{1/2} = 3.52 \frac{RT}{nF} \quad (3)$$

where F is the Faraday constant; R is the gas constant, $8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; T is the temperature in Kelvin.

From Fig. 3(a)–(e), n was calculated by Eq. (3) as follows: peak R_1 , $n \approx 1$; peak R_2 , $n \approx 2$; peak R_3 , $n \approx 3$. Thus, it suggests that the cathodic reaction of titanium ions takes place in two steps when $\alpha \leq 2.0$:



However, it transferred to a one-step reduction when $\alpha > 2.0$:



The redox potentials from Fig. 2 (CV) and Fig. 3 (SWV)

3. Results and discussion

3.1. Reduction of $TiCl_3$ in molten NaCl–KCl under various α

Fig. 2 shows the CV curves of titanium ions in the NaCl–KCl molten salt under different α conditions. Two pairs of redox peaks (O_1/R_1 , O_2/R_2) were observed in Fig. 2(a)–(c), while only one pair of redox peaks (O_3/R_3) was observed in Fig. 2(d) and (e). The results demonstrate that the reduction steps of Ti(III) convert from two steps to one step with the addition of KF.

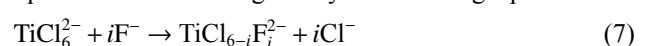
are listed in Table 1.

By measuring the open circuit potential (OCP), the recorded equilibrium potential of each KF addition was obtained. A typical OCP recorded under different α conditions (Fig. 4) shows that accurate measurements of the potential of the Ti(IV)→Ti(III) system can be achieved during the stability period. As can be seen from Fig. 4(a), the potential curve after 3000 s is nearly flat, and the curve after straight line fitting is shown in Fig. 4(b). It can be found that when α is 0.0, 1.0, 2.0, 3.0, and 5.0, the potentials correspond to -0.894 , -0.921 , -0.963 , -0.980 , and -0.993 V , respectively.

3.2. Mathematical analysis

In order to estimate the properties of the complex Ti–F, a mathematical analysis of the evolution of redox equilibrium potential was carried out based on the combination of the mass balance, thermodynamic equilibria, and Nernst relations.

Ti(IV), Ti(III), and Ti(II) are assumed to form several complexes between $TiCl_6^{2-}/TiCl_6^{3-}/TiCl_6^{4-}$ and F^- ions. The replacement reaction is given by the following equilibria:



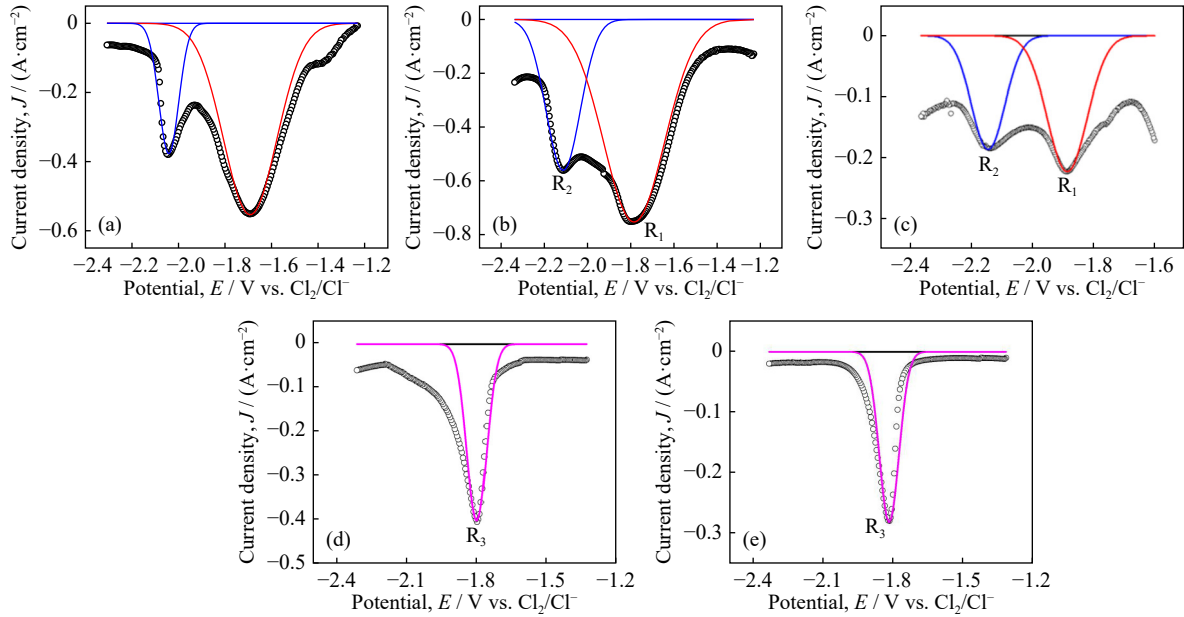


Fig. 3. Square wave voltammogram of titanium ions in NaCl–KCl melt on the glassy carbon electrode at various α values: (a) $\alpha = 0$; (b) $\alpha = 1.0$; (c) $\alpha = 2.0$; (d) $\alpha = 3.0$; (e) $\alpha = 5.0$. Frequency: 20 Hz; RE: Cl_2/Cl^- ; CE: graphite.

Table 1. Electrode redox potentials and reduction steps of titanium ions under various α

α	Redox peak potentials / V			Reduction process
	O_1/R_1	O_2/R_2	O_3/R_3	
0	-1.47/-1.69	-1.71/-1.99	—	$\text{Ti(III)} \xrightarrow{\text{R}_1} \text{Ti(II)} \xrightarrow{\text{R}_2} \text{Ti}$
1.0	-1.53/-1.81	-1.84/-2.12	—	$\text{Ti(III)} \xrightarrow{\text{R}_1} \text{Ti(II)} \xrightarrow{\text{R}_2} \text{Ti}$
2.0	-1.65/-1.91	-1.87/-2.15	—	$\text{Ti(III)} \xrightarrow{\text{R}_1} \text{Ti(II)} \xrightarrow{\text{R}_2} \text{Ti}$
3.0	—	—	-1.41/-1.79	$\text{Ti(III)} \xrightarrow{\text{R}_3} \text{Ti}$
5.0	—	—	-1.49/-1.82	$\text{Ti(III)} \xrightarrow{\text{R}_3} \text{Ti}$

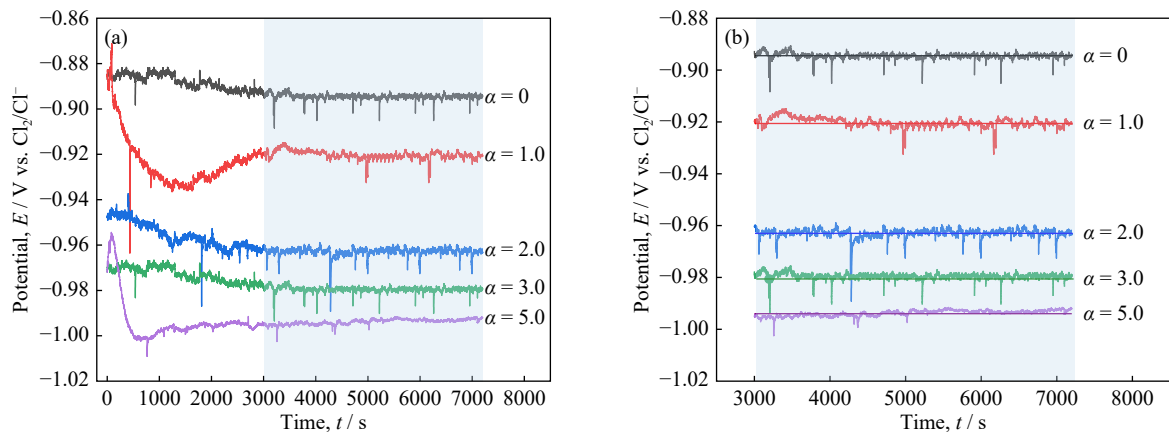
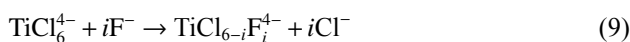
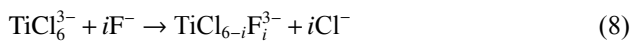


Fig. 4. OCP curves (in range of 3000–7200 s) obtained at various α values: (a) actual curve; (b) fitted curve.



The activity is defined as [34–36]:

$$\alpha_{\text{TiCl}_6^{2-}, \text{F}} = \frac{[\text{Ti(IV)}]_{\text{T}}}{[\text{TiCl}_6^{2-}]} \quad (10)$$

$$\alpha_{\text{TiCl}_6^{3-}, \text{F}} = \frac{[\text{Ti(III)}]_{\text{T}}}{[\text{TiCl}_6^{3-}]} \quad (11)$$

$$\alpha_{\text{TiCl}_6^{4-}, \text{F}} = \frac{[\text{Ti(II)}]_{\text{T}}}{[\text{TiCl}_6^{4-}]} \quad (12)$$

In the Eqs. (10)–(12), $[\text{TiCl}_6^{2-}]$, $[\text{TiCl}_6^{3-}]$, and $[\text{TiCl}_6^{4-}]$ are the concentration of Ti(IV), Ti(III), and Ti(II) cations which do not coordinate with F^- , and $[\text{Ti(IV)}]_{\text{T}}$, $[\text{Ti(III)}]_{\text{T}}$, and $[\text{Ti(II)}]_{\text{T}}$ are the total concentration of Ti(IV), Ti(III), and Ti(II) (coordinating and non-coordinating with F^-), respectively. Then, Eqs. (10)–(12) can be transformed into Eqs. (13)–(15).

$$\alpha_{\text{TiCl}_6^{2-},\text{F}} = 1 + \sum_{i=1}^x \frac{[\text{TiCl}_{6-i}\text{F}_i^{2-}]}{[\text{TiCl}_6^{2-}]} \quad (13)$$

$$\alpha_{\text{TiCl}_6^{3-},\text{F}} = 1 + \sum_{i=1}^x \frac{[\text{TiCl}_{6-i}\text{F}_i^{3-}]}{[\text{TiCl}_6^{3-}]} \quad (14)$$

$$\alpha_{\text{TiCl}_6^{4-},\text{F}} = 1 + \sum_{i=1}^x \frac{[\text{TiCl}_{6-i}\text{F}_i^{4-}]}{[\text{TiCl}_6^{4-}]} \quad (15)$$

where $\text{TiCl}_{6-i}\text{F}_i^{2-}$, $\text{TiCl}_{6-i}\text{F}_i^{3-}$, and $\text{TiCl}_{6-i}\text{F}_i^{4-}$ are the coordination forms of titanium ions with chloride and fluorine ions; $[\text{TiCl}_{6-i}\text{F}_i^{2-}]$, $[\text{TiCl}_{6-i}\text{F}_i^{3-}]$, and $[\text{TiCl}_{6-i}\text{F}_i^{4-}]$ are the concentrations of Ti(IV), Ti(III), and Ti(II) cations coordinating with Cl^- and F^- at each fluoride concentration, respectively; $1 \leq x \leq 6$.

Associate with the cumulative complexation constants β_i :

$$\beta_i = \frac{[\text{TiCl}_{6-i}\text{F}_i^{2-}][\text{Cl}^-]^i}{[\text{TiCl}_6^{2-}][\text{F}^-]_{\text{free}}^i} \quad (16)$$

$$\beta_i = \frac{[\text{TiCl}_{6-i}\text{F}_i^{3-}][\text{Cl}^-]^i}{[\text{TiCl}_6^{3-}][\text{F}^-]_{\text{free}}^i} \quad (17)$$

$$\beta_i = \frac{[\text{TiCl}_{6-i}\text{F}_i^{4-}][\text{Cl}^-]^i}{[\text{TiCl}_6^{4-}][\text{F}^-]_{\text{free}}^i} \quad (18)$$

where $[\text{F}^-]_{\text{free}}$ is the concentration of free fluoride ions, and $[\text{Cl}^-]$ is the concentration of free chloride ions.

Then, Eqs. (16)–(18) can be transformed into Eqs. (19)–(21):

$$\frac{[\text{TiCl}_{6-i}\text{F}_i^{2-}]}{[\text{TiCl}_6^{2-}]} = \frac{\beta_i[\text{F}^-]_{\text{free}}^i}{[\text{Cl}^-]^i} \quad (19)$$

$$\frac{[\text{TiCl}_{6-i}\text{F}_i^{3-}]}{[\text{TiCl}_6^{3-}]} = \frac{\beta_i[\text{F}^-]_{\text{free}}^i}{[\text{Cl}^-]^i} \quad (20)$$

$$\frac{[\text{TiCl}_{6-i}\text{F}_i^{4-}]}{[\text{TiCl}_6^{4-}]} = \frac{\beta_i[\text{F}^-]_{\text{free}}^i}{[\text{Cl}^-]^i} \quad (21)$$

Then combining the Eqs. (13)–(15) and (19)–(21), complexation coefficient can be expressed by:

$$\alpha_{\text{TiCl}_6^{2-},\text{F}} = 1 + \sum_{i=1}^x \frac{\beta_i[\text{F}^-]_{\text{free}}^i}{[\text{Cl}^-]^i} \quad (22)$$

$$\alpha_{\text{TiCl}_6^{3-},\text{F}} = 1 + \sum_{i=1}^x \frac{\beta_i[\text{F}^-]_{\text{free}}^i}{[\text{Cl}^-]^i} \quad (23)$$

$$\alpha_{\text{TiCl}_6^{4-},\text{F}} = 1 + \sum_{i=1}^x \frac{\beta_i[\text{F}^-]_{\text{free}}^i}{[\text{Cl}^-]^i} \quad (24)$$

Since the concentration of Cl^- is much higher than that of Ti(IV), Ti(III), Ti(II), and F^- in molten salt, $[\text{Cl}^-]$ can be approximated as a constant, and it can be assumed to k_i :

$$k_i = \frac{\beta_i}{[\text{Cl}^-]^i} \quad (25)$$

Then, Eqs. (22)–(24) can be rewritten as Eqs. (26)–(28), in which $[\text{F}^-]_{\text{T}}$ is the total concentration of F^- ions introduced, and it can be approximated as: $[\text{F}^-]_{\text{free}} = [\text{F}^-]_{\text{T}}$.

$$\alpha_{\text{TiCl}_6^{2-},\text{F}} = 1 + \sum_{i=1}^x k_i [\text{F}^-]_{\text{T}}^i \quad (26)$$

$$\alpha_{\text{TiCl}_6^{3-},\text{F}} = 1 + \sum_{i=1}^x k_i [\text{F}^-]_{\text{T}}^i \quad (27)$$

$$\alpha_{\text{TiCl}_6^{4-},\text{F}} = 1 + \sum_{i=1}^x k_i [\text{F}^-]_{\text{T}}^i \quad (28)$$

The complexation coefficient can be deduced from the measurement of equilibrium potentials before and after addition of fluoride ions in the molten salt. The Nernst equation is given by:

$$E_{0,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}} = E_{\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{[\text{TiCl}_6^{2-}]}{[\text{TiCl}_6^{3-}]} \right) \quad (29)$$

$$E_{0,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}} = E_{\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{[\text{TiCl}_6^{3-}]}{[\text{TiCl}_6^{4-}]} \right) \quad (30)$$

$$E_{0,\text{TiCl}_6^{4-}/\text{Ti}} = E_{\text{TiCl}_6^{4-}/\text{Ti}}^{\ominus} + \frac{2.3RT}{nF} \lg [\text{TiCl}_6^{4-}] \quad (31)$$

After coordination with F^- ions, the Eqs. (29)–(31) and can be written as:

$$E_{i,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}} = E_{\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{[\text{TiCl}_6^{2-}]_i}{[\text{TiCl}_6^{3-}]_i} \right) \quad (32)$$

$$E_{i,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}} = E_{\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{[\text{TiCl}_6^{3-}]_i}{[\text{TiCl}_6^{4-}]_i} \right) \quad (33)$$

$$E_{i,\text{TiCl}_6^{4-}/\text{Ti}} = E_{\text{TiCl}_6^{4-}/\text{Ti}}^{\ominus} + \frac{2.3RT}{nF} \lg [\text{TiCl}_6^{4-}]_i \quad (34)$$

where $E_{0,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}$, $E_{0,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}$, and $E_{0,\text{TiCl}_6^{4-}/\text{Ti}}$ are the initial equilibrium potential (E_{eq}) of Ti(IV), Ti(III), and Ti(II) before adding fluoride ions; $E_{\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}^{\ominus}$, $E_{\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}^{\ominus}$, and $E_{\text{TiCl}_6^{4-}/\text{Ti}}^{\ominus}$ are the standard potential of Ti(IV), Ti(III), and Ti(II); $[\text{TiCl}_6^{2-}]_i$, $[\text{TiCl}_6^{3-}]_i$, and $[\text{TiCl}_6^{4-}]_i$ are the concentration of Ti(IV), Ti(III), and Ti(II) cations which do not coordinate with F^- at each fluoride concentration; $E_{i,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}$, $E_{i,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}$, and $E_{i,\text{TiCl}_6^{4-}/\text{Ti}}$ are the equilibrium potential of Ti(IV), Ti(III), Ti(II) at each fluoride concentration. These values can be calculated by CV, SWV, and OCP mentioned above, where:

$$E_{\text{eq}} = E_{1/2} = (E_C + E_A)/2 \quad (35)$$

where E_C , E_A , and $E_{1/2}$ are cathode peak potential, anode peak potential, and half-peak potential, respectively [37].

Combining Eqs. (10)–(12) and Eqs. (32)–(34), the following relationship can be obtained:

$$E_{i,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}} = E_{\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{\alpha_{\text{TiCl}_6^{2-},\text{F}} [\text{Ti(IV)}]_{\text{T}}}{\alpha_{\text{TiCl}_6^{3-},\text{F}} [\text{Ti(III)}]_{\text{T}}} \right) \quad (36)$$

$$E_{i,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}} = E_{\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{\alpha_{\text{TiCl}_6^{3-},\text{F}} [\text{Ti(III)}]_{\text{T}}}{\alpha_{\text{TiCl}_6^{4-},\text{F}} [\text{Ti(II)}]_{\text{T}}} \right) \quad (37)$$

$$E_{i,\text{TiCl}_6^{4-}/\text{Ti}} = E_{\text{TiCl}_6^{4-}/\text{Ti}}^{\ominus} + \frac{2.3RT}{nF} \lg \left(\frac{[\text{Ti(II)}]_{\text{T}}}{\alpha_{\text{TiCl}_6^{4-},\text{F}}} \right) \quad (38)$$

Subtracting the Eqs. (36)–(38) and Eqs. (29)–(31), then we can obtain Eqs. (39)–(44):

$$E_{i,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}} - E_{0,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}} = \frac{2.3RT}{nF} \left[\lg \left(\frac{\alpha_{\text{TiCl}_6^{2-},\text{F}} [\text{Ti(IV)}]_{\text{T}}}{\alpha_{\text{TiCl}_6^{3-},\text{F}} [\text{Ti(III)}]_{\text{T}}} \right) - \lg \left(\frac{[\text{Ti(IV)}]_{\text{T}}}{[\text{Ti(III)}]_{\text{T}}} \right) \right] \quad (39)$$

$$E_{i,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}} - E_{0,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}} = \frac{2.3RT}{nF} \left[\lg \left(\frac{\alpha_{\text{TiCl}_6^{3-},\text{F}} [\text{Ti(III)}]_{\text{T}}}{\alpha_{\text{TiCl}_6^{4-},\text{F}} [\text{Ti(II)}]_{\text{T}}} \right) - \lg \left(\frac{[\text{Ti(III)}]_{\text{T}}}{[\text{Ti(II)}]_{\text{T}}} \right) \right] \quad (40)$$

$$E_{i,\text{TiCl}_6^{4-}/\text{Ti}} - E_{0,\text{TiCl}_6^{4-}/\text{Ti}} = \frac{2.3RT}{nF} \left[\lg \left(\frac{[\text{Ti(II)}]_{\text{T}}}{\alpha_{\text{TiCl}_6^{4-},\text{F}}} \right) - \lg [\text{Ti(II)}]_{\text{T}} \right] \quad (41)$$

$$\lg \alpha_{\text{TiCl}_6^{2-},\text{F}} = \frac{nF}{2.3RT} (E_{0,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}} - E_{i,\text{TiCl}_6^{2-}/\text{TiCl}_6^{3-}}) + \lg \alpha_{\text{TiCl}_6^{2-},\text{F}} \quad (42)$$

$$\lg \alpha_{\text{TiCl}_6^{3-},\text{F}} = \frac{nF}{2.3RT} (E_{0,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}} - E_{i,\text{TiCl}_6^{3-}/\text{TiCl}_6^{4-}}) + \lg \alpha_{\text{TiCl}_6^{3-},\text{F}} \quad (43)$$

$$\lg \alpha_{\text{TiCl}_6^{4-},\text{F}} = \frac{nF}{2.3RT} (E_{0,\text{TiCl}_6^{4-}/\text{Ti}} - E_{i,\text{TiCl}_6^{4-}/\text{Ti}}) \quad (44)$$

According to Table 2, the experiment values of $\lg \alpha_{\text{TiCl}_6^{4-},\text{F}}$, $\lg \alpha_{\text{TiCl}_6^{3-},\text{F}}$, and $\lg \alpha_{\text{TiCl}_6^{2-},\text{F}}$ vs. $\lg [\text{F}^-]_{\text{T}}$ are shown in Fig. 5. The slope equals to 0.99 for $\lg \alpha_{\text{TiCl}_6^{4-},\text{F}}$ and $\lg [\text{F}^-]_{\text{T}}$. This shows that the number of F^- coordinated with Ti(II) is close to 1.0. The slope changes from 2.46 to 4.04 with fluoride ions increases for $\lg \alpha_{\text{TiCl}_6^{3-},\text{F}}$ and $\lg [\text{F}^-]_{\text{T}}$. In the same way, it changes from 1.83 to 4.23 for $\lg \alpha_{\text{TiCl}_6^{2-},\text{F}}$ and $\lg [\text{F}^-]_{\text{T}}$. This indicates that the number of F^- coordinated with Ti(III) and Ti(IV) increases with the addition of fluoride ions.

Table 2. Values of $\lg [\text{F}^-]_{\text{T}}$, $\lg \alpha_{\text{TiCl}_6^{4-},\text{F}}$ at different α conditions

α	Molar mass of KF, C_{KF} / ($\text{mol} \cdot \text{kg}^{-1}$)	$\lg [\text{F}^-]_{\text{T}}$	$\lg \alpha_{\text{TiCl}_6^{4-},\text{F}}$	$\lg \alpha_{\text{TiCl}_6^{3-},\text{F}}$	$\lg \alpha_{\text{TiCl}_6^{2-},\text{F}}$
1.0	0.21	-0.68	1.282	1.73	1.92
2.0	0.42	-0.38	1.578	2.47	2.47
3.0	0.63	-0.20	—	0.29	0.69
5.0	1.05	0.02	—	1.18	1.62

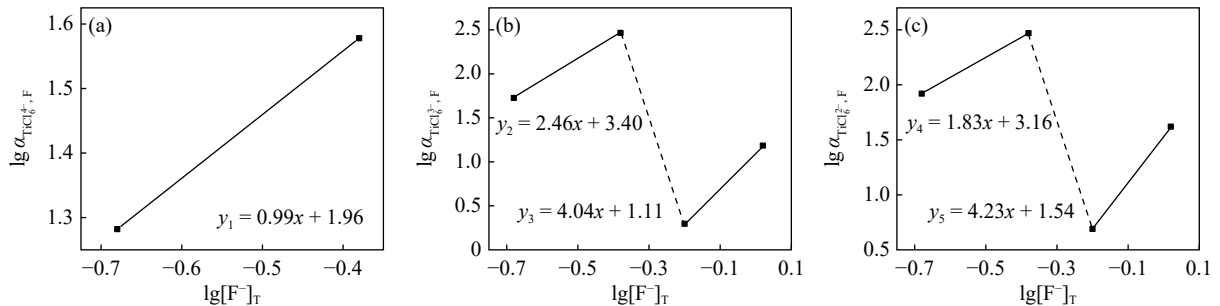


Fig. 5. Plot of $\lg \alpha_{\text{TiCl}_6^{4-},\text{F}}$, $\lg \alpha_{\text{TiCl}_6^{3-},\text{F}}$, and $\lg \alpha_{\text{TiCl}_6^{2-},\text{F}}$ vs. $\lg [\text{F}^-]_{\text{T}}$.

3.3. Spectral analysis

Fig. 6 shows sample images under the condition of various α . It can be found that the color of the sample changed significantly when α varied from 0 to 8.0. Literature shows that Ti^{2+} , Ti^{3+} , and Ti^{4+} display colors were emerald green, reddish brown, and colorless, respectively [22]. The color variation trend in the Fig. 6 indicates the average valence of titanium ion changes in molten salt. It was emerald green with free of fluoride, indicating the color of Ti^{2+} . According to the distribution of titanium ions measured above, it can be

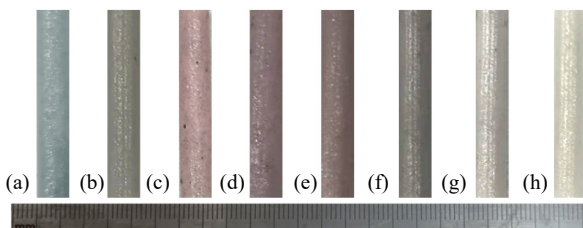


Fig. 6. Samples under different α in NaCl–KCl molten salt at 1023 K: (a) 0; (b) 1.0; (c) 2.0; (d) 3.0; (e) 4.0; (f) 5.0; (g) 6.0; (h) 8.0.

concluded that the Ti^{3+} takes up to 53.86wt% of titanium ions, mainly because Ti^{2+} is green and has serious color-rendering, which will cover up the reddish brown of Ti^{3+} .

When the concentration of fluoride increases, the color of sample gradually changes from green to reddish brown and then gradually becomes light to colorless. It shows that Ti^{2+} in molten salt disappears gradually, Ti^{3+} is the main body, and finally titanium ions are converted into Ti^{4+} . Schematic diagram of equilibrium mechanism shows in Fig. 1(b).

Fig. 7(a) is the image of molten salt containing titanium ions before adding fluoride ($\alpha = 0$), and Fig. 7(b) shows the macroscopic view of molten salt after salt extraction at $\alpha = 8.0$. The color changed from green to light, which further confirmed that the addition of fluoride has a great influence on the ratio of titanium ions with different valence states in molten salt.

It can be observed that the color is much light for the samples in Fig. 6. It may be due to the sample was taken out *in-situ* (at a high temperature), while the darker color after condensation in Fig. 7 is caused by the shift of titanium ion balance when low-down the temperature. According to liter-

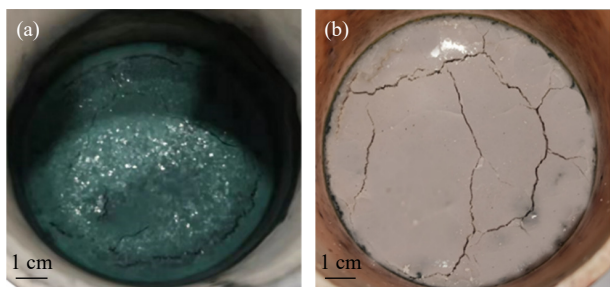


Fig. 7. (a) Image of molten salt containing titanium ions before adding fluoride ion ($\alpha = 0$); (b) macroscopic view of molten salt at $\alpha = 8.0$.

ature reported [3], the disproportionation reaction will move in the direction of divalent titanium at a low temperature. As a result, the color of the sample differs from that of the condensate.

XPS analysis was carried out to further study the complexation equilibrium relationship between titanium and fluoride ions at different fluoride ion concentrations, and XPS analysis results of samples with different fluoride ion concentrations are shown in Fig. 8. As refer to database of XPS, the blue part bond energy is 456 eV, which is the characterization energy of Ti^{2+} ; the bond energy of pink part is 458.2 eV, which is the characterization energy of Ti^{3+} ; the green bond energy is 459.8 eV, which is the characterization energy of Ti^{4+} [38–39]. According to the Fig. 8, three peaks can be fitted when no fluoride ion was added, and XPS fitting results show that Ti^{2+} , Ti^{3+} , and Ti^{4+} are mixed in molten salt. When fluoride was added, the blue area in the fitted curve decreased gradually, indicating that concentration of Ti^{2+} gradually decreased. When $\alpha = 3.0$, blue area basically disappeared which means the Ti^{2+} vanishes in the melt. The pink part in Fig. 8 first increases and then decreases, it indicates

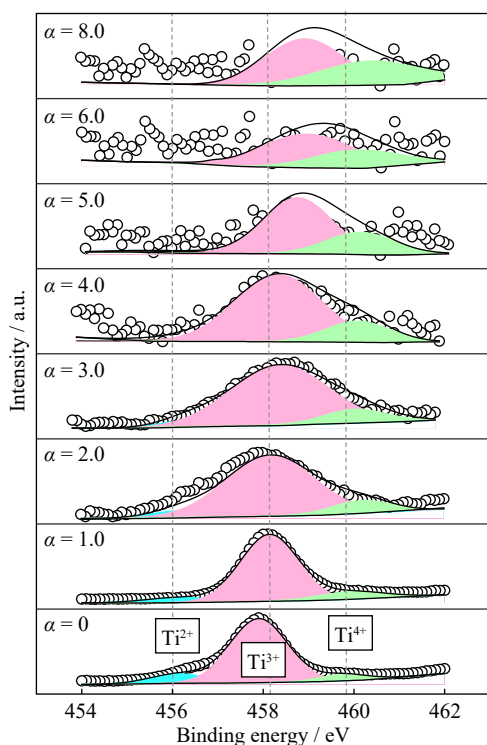
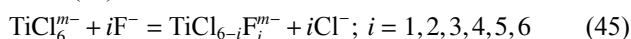


Fig. 8. XPS patterns of samples under different α conditions.

that concentration of Ti^{3+} in the melt increases and then decreases with adding of fluoride. Moreover, the XPS diagram moves to the right as a whole, and the green area in the fitting peak gradually increases with the increase of fluoride ion concentration, indicating that Ti^{4+} ions in the melt gradually increases. In this process, it can be shown that the introduction of fluoride ions is beneficial for stabilizing a titanium ion in high-valence. When $\alpha = 3.0$, Ti^{2+} ions cannot be detected in the molten salt, and thus the ion balance is maintained between Ti , Ti^{3+} , and Ti^{4+} . The above test and analysis results are consistent with the macroscopic images of the samples in Fig. 6.

As described before, the disproportionation reactions (1) and (2) occurred between metallic titanium and titanium ions in molten salt. The coordination ratio of fluoride and titanium ions will transfer the equilibrium reaction, and thus affect the existence state of titanium ions in molten salt, besides, the variation of XPS peaks can be described by replacement reaction (45).



The results show that the change of the equilibrium of disproportionation reaction results from fluoride addition mainly because of the complexation of fluoride with high-valence state titanium ion. Eventually, the equilibrium of bivalent titanium and trivalent titanium will shift toward trivalent titanium, and the trivalent titanium and tetravalent titanium will transfer to tetravalent titanium.

To further verify the specific morphology of coordination compounds of fluoride and titanium ions, samples under various α conditions were analyzed by Raman spectroscopy, and the results are shown in Fig. 9.

When $\alpha = 0$, there are three characteristic peaks in the Raman spectrum, which are 489, 713, and 944 cm^{-1} , which corresponded to the complexes $TiCl_6^{2-}$, $TiCl_6^{4-}$, and $TiCl_6^{3-}$, respectively. It can also be found that when $\alpha = 1.0$, additional peak at 611 cm^{-1} is observed. It indicates that titanium ions and newly added fluoride ions formed a new complex: $TiCl_5F^{3-}$. When $\alpha = 2.0$, there are three peaks, and new characteristic peaks of $TiCl_5F^{4-}$, $TiCl_5F^{2-}$, and $TiCl_4F_2^{3-}$ appears at 413, 540, and 887 cm^{-1} , respectively, while the $TiCl_6^{2-}$, $TiCl_6^{4-}$, $TiCl_5F^{3-}$, and $TiCl_6^{3-}$ peaks no longer exist. However, when $\alpha = 3.0$, $TiCl_5F^{4-}$ peak disappears. When $\alpha = 4.0$, there are three peaks, and a new peak $TiCl_3F_3^{3-}$ appears at 519 cm^{-1} . When α is in the range of 5.0 to 8.0, there are five peaks, $TiCl_4F_2^{3-}$ peak disappears, and new peaks of $TiCl_2F_4^{3-}$, $TiCl_4F_2^{2-}$, and TiF_6^{2-} appear at 295, 342, and 918 cm^{-1} , respectively. However, with the increase of fluoride ion, the peak strength changes, $TiCl_3F_3^{3-}$ peak strength decreases, and TiF_6^{2-} strength increases. The above results are summarized in Table 3.

Titanium ions exist as complexions in molten chloride salts: $TiCl_i^{m-}$. Due to the existence of different valence states of titanium ions, disproportionation reaction will occur in the intermediate valence state of titanium ions. When a certain amount of fluoride ion is added to the electrolyte, $TiCl_i^{m-}$ will undergo replacement reaction with fluoride ions through reactions (46)–(53), resulting in a right shift in the equilibrium of reaction (2). It can also be explained by the schematic dia-

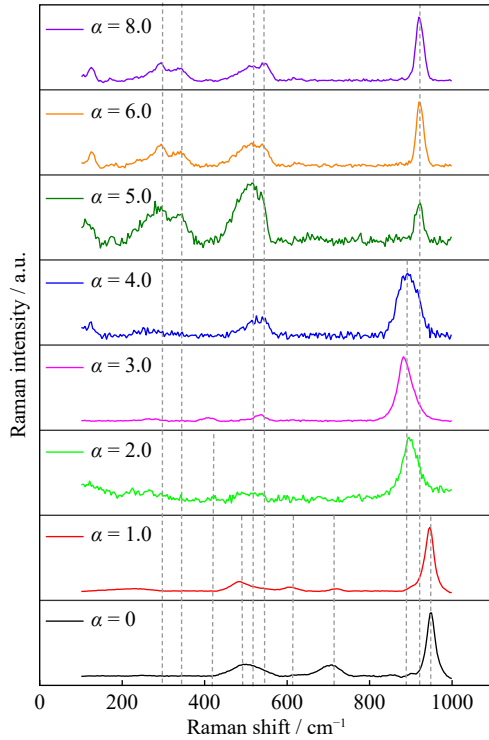


Fig. 9. Raman spectra of samples under different α values.

gram of equilibrium mechanism in Fig. 1(b). The reason is that compared with chloride ion, fluoride ion has a smaller ionic radius and is easier to replace chloride ion forming a coordination relationship with titanium ion in molten salt [40–41]. Thus, in molten salts containing titanium ions, fluoride ions form a coordination compound with titanium ions: $\text{TiCl}_j\text{F}_i^{m-}$.

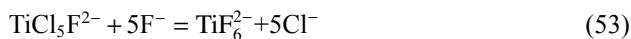
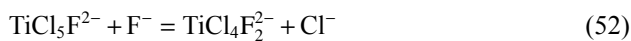
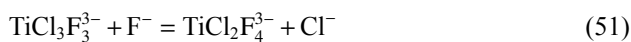
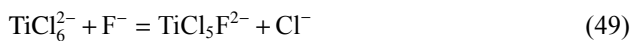
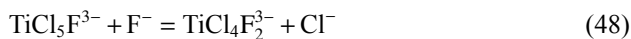
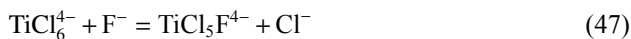
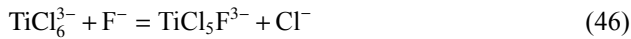


Table 3. Raman peaks and possible types of complexes under various α ($\alpha = 0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, \text{ and } 8.0$)

α	Possible types of complexes				
0	TiCl_6^{2-}	TiCl_6^{4-}	TiCl_6^{3-}	—	—
1.0	TiCl_6^{2-}	TiCl_6^{4-}	$\text{TiCl}_5\text{F}^{3-}$	TiCl_6^{3-}	—
2.0	$\text{TiCl}_5\text{F}^{4-}$	$\text{TiCl}_5\text{F}^{2-}$	$\text{TiCl}_4\text{F}_2^{3-}$	—	—
3.0	$\text{TiCl}_5\text{F}^{2-}$	$\text{TiCl}_4\text{F}_2^{3-}$	—	—	—
4.0	$\text{TiCl}_3\text{F}_3^{3-}$	$\text{TiCl}_5\text{F}^{2-}$	$\text{TiCl}_4\text{F}_2^{3-}$	—	—
5.0	$\text{TiCl}_2\text{F}_4^{3-}$	$\text{TiCl}_4\text{F}_2^{2-}$	$\text{TiCl}_3\text{F}_3^{3-}$	$\text{TiCl}_5\text{F}^{2-}$	TiF_6^{2-}
6.0	$\text{TiCl}_2\text{F}_4^{3-}$	$\text{TiCl}_4\text{F}_2^{2-}$	$\text{TiCl}_3\text{F}_3^{3-}$	$\text{TiCl}_5\text{F}^{2-}$	TiF_6^{2-}
8.0	$\text{TiCl}_2\text{F}_4^{3-}$	$\text{TiCl}_4\text{F}_2^{2-}$	$\text{TiCl}_3\text{F}_3^{3-}$	$\text{TiCl}_5\text{F}^{2-}$	TiF_6^{2-}

The formation of these coordination compounds makes the equilibrium of titanium ions transformed. Titanium free ions existed as Ti^{2+} , Ti^{3+} , and Ti^{4+} in molten salt without adding fluoride ions. Ti^{2+} disappeared and titanium ion mainly existed as Ti^{3+} and Ti^{4+} complexes after fluoride ion is added. The Raman analysis and XPS results perfectly reveal the phenomenon and mechanism.

4. Conclusion

In this research, electrochemical and mathematical analysis as well as spectral techniques were performed to investigate the effect of fluoride ions on the coordination structure of titanium ions in NaCl–KCl molten salt. The coordination mechanism of Ti–F under various fluoride ion content was obtained. It showed that fluoride ions can reduce the reduction steps of titanium ions and greatly affect the proportion of titanium ions' valence states, and the average valence of titanium ions increased with the increasing of proportion of fluoride ions. The Raman analysis and XPS results showed that when $\alpha = 3.0$, Ti^{2+} cannot be detected in the molten salt, and finally existed mainly as coordination compounds with fluoride ions: $\text{TiCl}_j\text{F}_i^{m-}$.

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Conflict of Interests

The authors declare no conflict of interest.

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