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Chapter

Effect of Electrolytic Compositions in Kinetics Mechanism of High-Purity Titanium Electrochemical Extraction Process

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Abstract

High pure titanium, which is a critical material used for integrated circuit (IC) manufacturing, can be extracted by molten salt-electrolysis process. It will be widely used in the future for the process, is simple and easy, to achieve continuous production. However, some scientific questions need to be clarified at present. (1) Current efficiency needs to be enhanced by way of electrolyte designing and selection; (2) Product quality needs to be improved by means of electrolyte purification; (3) Electrolytic parameters need to be optimized for obtaining a better morphology. Above on, this chapter aims to explore the behaviors of titanium ions in various molten salts by means of chemical analysis and electrochemical testing. The complexes will be discussed for clarifying the influence of electrolytic compositions on kinetics mechanisms of the electrolysis process and the properties of the molten salt. A quantitative method for estimating oxygen content will be also discussed for the purpose of optimizing the composition of electrolytes. The chapter will provide a better understanding mechanism of kinetics of high pure titanium electrolysis, and the basic theory and experimental data can be used for reference in the industrialization process.

Keywords: electrolysis, molten salt structures, kinetics mechanism, high-purity titanium

1. Introduction

High-purity titanium has excellent properties, such as light weight, corrosion resistance, and low electrical resistivity [1, 2]. It is mainly used in large-scale integrated circuit (IC) manufacturing, new type of titanium-alloy and other fields. Therefore, it is a strategic material for electronic and aerospace.

As a sputtering target for manufacturing large-scale IC, a purity of 4 N5 (99.995%) to 6 N (99.9999%) is required for titanium, in which the oxygen content is below 200 ppm, and the metal impurity content is less than 10 ppm. However, the current technology for preparing high-purity titanium has caused a high price, which directly leads to lacking of application in large scale. Thereby, the development of new methods and technologies to prepare high-quality and low-cost

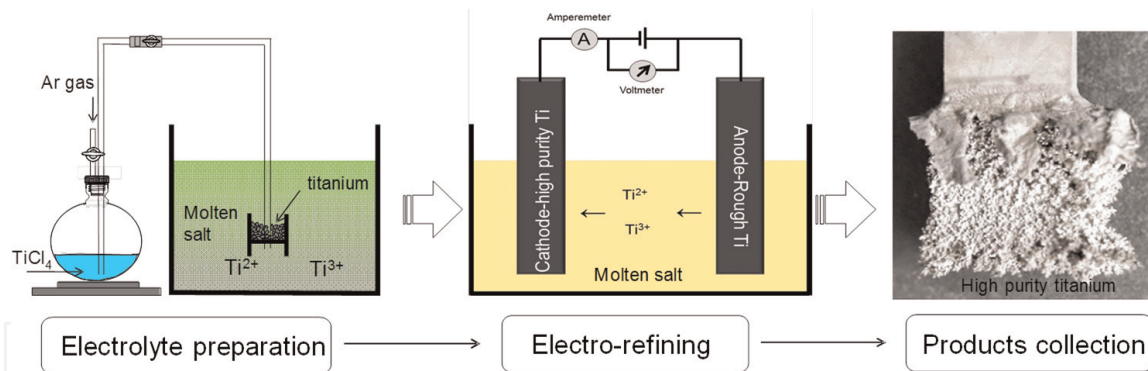


Figure 1.
Diagram of electro-refining process of high-purity titanium in molten salt.

titanium will greatly promote large-scale IC industry. Considering the preparation technology of high-purity titanium, the process of electro-refining in molten salt which is simple in process and easy to realize successive has a very broad application prospect, and has attracted much attention. The extraction process of high-purity titanium in molten salt is shown in **Figure 1**.

In the process, for the first step, TiCl_4 and high-purity titanium were used to react for obtaining a molten salt containing low-valent titanium ions (Ti^{2+} and Ti^{3+}). The salt will be used as a source of titanium ions to be added to the eutectic salt. Second, titanium sponge which comes from Kroll process is used as anode, and a high-purity titanium plate is used for cathode. During the working of electrolysis, the anode is electrochemically dissolved and the electrochemical deposition of high-purity titanium occurs on the cathode. Finally, high-purity titanium products with different morphology and quality are obtained under different electrolysis parameters.

At present, the problems that need to be solved in the industrialization process of high-purity titanium extraction with the method of electro-refining in molten salt are below: (a) current efficiency need to be improved; (b) product qualities should be enhanced. Since the existence of various state of titanium ions in the molten salt (Ti^{2+} , Ti^{3+} , and Ti^{4+}), the disproportionation reactions between titanium ions and the metallic titanium cause a current consumption. Thus, it is critical to reveal the behavior of titanium ions in different electrolyte compositions/structures for improving current efficiency. In addition, oxygen has a great influence on the quality of the product, and the oxygen ions in the electrolyte cannot be completely removed. It is of great practical significance to discuss the influence of oxygen ions on the structure of the molten salt for enhancing the product quality. With a better understanding of the kinetics in titanium electrolysis process on the basis of systematic investigation of electrolyte microstructures, it will provide theoretical guidance for high-purity titanium electro-refining process in molten salt, and has important reference value for its industrialization test.

In this chapter, it aims to explore the behaviors of titanium ions in various molten salts by means of chemical analysis and electrochemical testing. The complexes will be discussed for clarifying the influence of electrolytic compositions on kinetics mechanisms of the electrolysis process and the properties of the molten salt.

2. Experimental methods

2.1 Electrochemical analysis

The electrolyte was melted in the alumina crucible after being placed in a furnace. The electrochemical analyses, such as cyclic voltammetry (CV), square

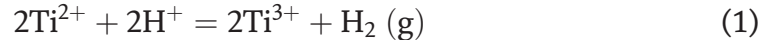
wave voltammetry (SWV), line scanning voltammetry (LSV), and so on, were performed in an inert argon atmosphere previously dehydrated by heating in a vacuum. All measurements were carried out under the atmosphere of dried argon. In order to investigate the influence of the radius of the cations and fluoride ion in the melts, analyses were executed in various types of molten salts.

All the electrochemical tests were carried out in a three-electrodes configuration with a glassy carbon or metallic rod/disk being the working electrode, a spectral graphite rod being counter electrode, and an Ag/AgCl electrode or metallic titanium rod being the reference electrode, respectively. Sometimes, the potential of the reference electrode was calibrated relative to chlorine gas emission by using galvanic square wave technology.

In addition, during the electrochemical testing, the gas was analyzed on line with a resolution mass spectra and a high-sensitivity gas analysis instrument connected to the electrode tail tubing. The gas-collecting device was made with a quartz bell jar, and it correlates with resolution mass spectra, and high-purity helium was used as a carrier gas.

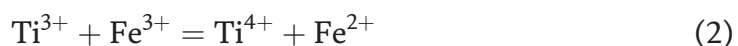
2.2 Concentration determination

A special quartz sampler consisting of an injector and a quartz tube was applied for determining the concentrations of Ti^{2+} and Ti^{3+} ions. The injector on top of the quartz tube is sealed with a rubber plug. Four parallel samples were extracted from the molten salts for analysis. The concentrations of Ti^{2+} and Ti^{3+} ions in the sample were determined by H_2 volumetric analysis and titration, respectively. According to reaction (1), the concentration of Ti^{2+} was quantified by H_2 volumetric analysis.



It is worth noting that that the dissolved oxygen in an aqueous solution will oxidize titanium ions from Ti^{2+} into Ti^{3+} , which is also the reason why the concentration of Ti^{2+} ions is underestimated. Thus, the deionized water was treated by vacuum degassing and completely cleaned by the high-purity argon gas. A specific amount of concentrated hydrochloric acid was injected into the deoxygenized water to prepare diluted hydrochloric acid (1 mol/L). The deoxygenized hydrochloric acid solution was saturated by bubbling high-purity H_2 for 30 min to prevent the evolution of H_2 by reaction (1).

Note that the concentration of Ti^{3+} ions in the solution consisted of the initial Ti^{3+} ions in the sample and the oxidized Ti^{3+} ions. The total concentration of Ti^{3+} ions in the solution was determined by titration using 0.05 mol/L $NH_4Fe(SO_4)_2$ aqueous solution. The Ti^{3+} in the solution reacted with Fe^{3+} follow by reaction (2).



Finally, the concentration of Ti^{4+} from reaction (2) was determined by diantipyryl methane spectrophotometry, the concentration of Ti^{4+} was equal to the concentration of Ti^{2+} plus Ti^{3+} .

2.3 Electrochemical titration technique

The concentration of O^{2-} in the molten salt was determined by the P_O^{2-} indicator electrode consisted of a tube of Yttria Stabilized Zirconia (YSZ), and the reference electrode was an Ag/AgCl electrode. The auxiliary electrode was a spectrum

pure graphite rod. The variation of the YSZ electrode potential was recorded using the potentiostat.

The Nernstian behavior of the system was demonstrated by measuring the change in electrode potential. The relationship between the concentration of oxide and potential can be expressed as Eq. (3):

$$E_{O_2/O^{2-}} = E_{O_2/O^{2-}}^* - \frac{RT}{2F} P_{O_2} \quad (3)$$

where $E_{O_2/O^{2-}}$ is the equilibrium potential of O_2/O^{2-} system (in V); $E_{O_2/O^{2-}}^*$ is an apparent standard potential of the system (in V) and P_{O_2} is $(-\ln x_{O^{2-}})$; and $x_{O^{2-}}$ is the concentration of O^{2-} .

3. Results and discussion

3.1 Influence of electrolyte cation on ionic equilibrium of titanium

Metallic titanium and titanium ions undergo the following disproportionation reactions in the molten salt, and their equilibrium constants can be expressed by Eqs. (6) and (7), respectively [3, 4].



$$K_{c1} = \frac{x_{Ti^{3+}}^2 \cdot x_{Ti}}{x_{Ti^{2+}}^3} = \frac{x_{Ti^{3+}}^2}{x_{Ti^{2+}}^3} \quad (6)$$

$$K_{c2} = \frac{x_{Ti^{4+}}^3 \cdot x_{Ti}}{x_{Ti^{3+}}^4} = \frac{x_{Ti^{4+}}^3}{x_{Ti^{3+}}^4} \quad (7)$$

Titanium ions with various valent states will compete with host cations, such as alkali metal or alkaline earth metal ions when they are used as a cation to coordinate with a host anion (such as Cl^-) in molten salt. The coordination rules between titanium ions and anions will affect the direction of the above equilibrium reactions, thereby the existence of titanium ions in the molten salt will be changed. Moreover, the electrolysis process will be a one-step reduction of Ti^{2+} to Ti when titanium ions in the molten salt are stably present in form of Ti^{2+} . On the other hand, when Ti^{3+} or higher-valent titanium ions are stabilized, the electrolysis process will achieve a one-step reduction of Ti^{3+} to Ti. **Table 1** shows the reduction potentials of titanium ions in different chloride molten salts.

Results show that the reduction of titanium ions in above molten salts has undergone a two-step process of $Ti^{3+} \rightarrow Ti^{2+} \rightarrow Ti$ except CsCl-LiCl [5]. It can also be concluded that the smaller radius of the alkali metal or alkaline earth metal cation in the electrolyte, the stronger the coordination ability with the anion (Cl^-). Considering the mechanism in deep-layer, it can be interpreted that it is impossible to have enough Cl^- around Ti^{3+} in a molten with a smaller radius of the electrolyte. Then, the instability of Ti^{3+} in reaction (4) causes the reaction to move to the left, and the concentration of Ti^{2+} increases in the total concentration of titanium ions. When the average valence state of titanium ions in the molten salt is around 2.2–2.5, the electrolytic reduction of Ti^{3+} needs to undergo a process of $Ti^{3+} \rightarrow Ti^{2+} \rightarrow Ti$. On the contrary, when the average radius of electrolyte cation is larger, such as CsCl, Ti^{3+} is relatively stable, and the average valence state of titanium ions is about 2.7–2.9, which can realize one-step reduction of Ti^{3+} to Ti.

| Molten salt | $E_{\text{Ti}^{3+}/\text{Ti}^{2+}}$, V | $E_{\text{Ti}^{2+}/\text{Ti}}$, V | $E_{\text{Ti}^{3+}/\text{Ti}}$, V | Ref. electrode/Temp. |
|-------------------------------|---|------------------------------------|------------------------------------|--|
| CaCl ₂ | 0.20 [6] | -0.10 [6] | — | Ti, 1123 K [6] |
| CaCl ₂ -NaCl (1:1) | -0.85 [7] | -1.20 [7] | — | Ag ⁺ /Ag, 823 K [7] |
| LiCl-KCl (59:41) | -1.05 [8] | -1.68 [8] | — | Ag ⁺ /Ag, 723 K [8] |
| LiCl-KCl (59:41) | -1.78 [9] | -1.9 0 [9] | — | Cl ₂ /Cl ⁻ , 993 K [9] |
| CsCl-LiCl (59.5:40.5) | -1.88 [9] | -1.93 [9] | — | Cl ₂ /Cl ⁻ , 993 K [9] |
| CsCl-LiCl (59.5:40.5) | — | — | -2.01 [9] | Cl ₂ /Cl ⁻ , 793 K [9] |
| NaCl-KCl (1:1) | -1.75 [10] | -2.05 [10] | — | Cl ₂ /Cl ⁻ , 1023 K [10] |
| | 0.18 [11] | -0.18 [11] | — | Ti, 1023 K [11] |
| | -1.95 [9] | -1.98 [9] | — | Cl ₂ /Cl ⁻ , 993 K [9] |
| | 0.06 [12] | -0.06 [12] | — | Ti, 1006 K [12] |
| NaCl-CsCl (1:2) | -1.55 [13] | -1.80 [13] | — | Cl ₂ /Cl ⁻ , 873 K [13] |

Table 1.
 Reduction potentials in various chloride molten salt.

In order to deliberate the effect of cation in electrolyte, the relationship between K_c and cation radius was studied. It should be noted that the K_c are the final results and were analyzed by best-fitting method [14].

It was studied that the stability of chlorocomplexes is strongly affected by different solvent cations. One explanation may be described by a simple electrostatic model. Thus, it can be deduced that the titanium ions at their higher oxidation states are engaged in chlorocomplexes such as TiCl_4^- or TiCl_6^{3-} from the model. Moreover, there is a competition between alkali metal and titanium ions to associate with chloride ions. The smaller ionic radius of the alkali metal ions is, the more strongly associate with Cl^- , which results in a lesser stability of chlorocomplexes, and the stability of the Ti^{2+} complex increased in the presence of outer-sphere cations in the series Cs^+ to Li^+ . Under the circumstances, the maximum Ti^{2+} complex stability is achieved in the presence of Li^+ outer sphere cations.

For mixtures of alkali chlorides, the polarizing ability of alkali cations to Cl^- could be an average of each according to the mix ratio. Polarizing power is introduced for describing the numerous semi-quantitative relationships, involving the charge and the radius of the solvent cations can be present as follows:

$$P = \sum x_i \frac{Z_i}{r_i^2} \quad (8)$$

where the suffix i represents the solvent cation, Z_i is the charge of the cation, and r_i is the radius of it. The relationships between equilibrium constant and polarizing power is shown in **Figure 2**.

The values of K_c decreased with the enlargement of the polarizing power. The results also showed that the Ti^{3+} is less stable in the alkali chloride with a stronger polarizing power. A larger polarizing power of electrolyte results in a lesser stability of TiCl_6^{3-} and smaller K_c value. The stronger polarizing power is the closer of Cl^- combined with the alkali cation. More importantly, the K_c is a constant value when polarizing power is constant regardless in KCl-LiCl or CsCl-LiCl at 1023 K.

From the above, it can be concluded that the cation of electrolyte will impact on the equilibrium of disproportionation reactions (4) and (5). The reduction steps were revealed in various molten salt through electrochemical method, and the competition relationship between cation and titanium ion was also proved. Hence,

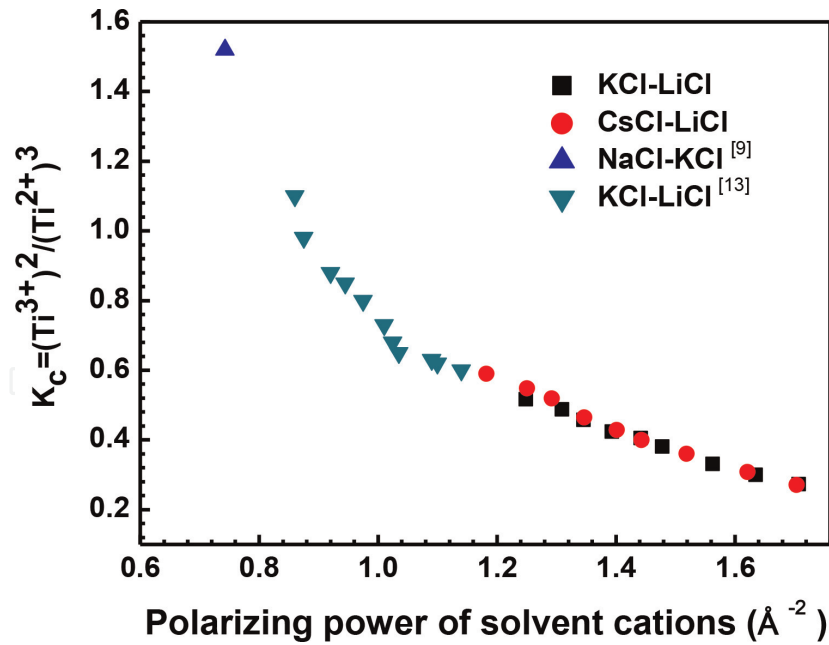


Figure 2.

The relationship between polarizing power of electrolyte and equilibrium constant at 1023 K (reprinted from Ref. [14]).

selecting one type of chloride molten salt in the high-purity titanium electro-refining process has great directive significance.

3.2 Influence of electrolyte anion on ionic equilibrium of titanium

3.2.1 Effect of fluoride ion on the state of titanium ions in molten salt

Relative to chloride ions, the ionic radius of fluoride ions is smaller, and it is easier to form a coordination relationship with the cations in the molten salt [14–19]. Therefore, coordination compounds, TiF_i^{n+} , will be formed between fluorine ions and titanium ions in a fluoride containing molten salt. The formation of these coordination compounds will effect on the valence equilibrium of titanium ions in the molten salt.

Figure 3 shows the variation of the apparent equilibrium constant of disproportionation

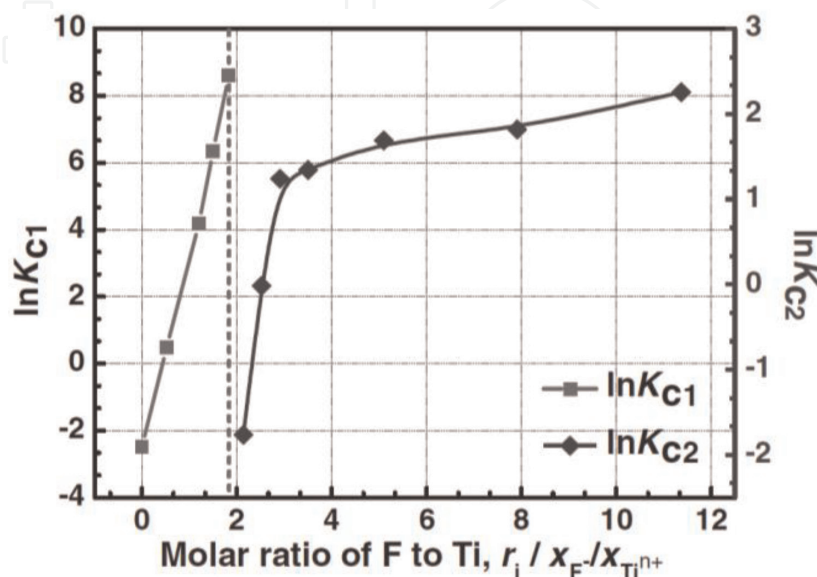


Figure 3.

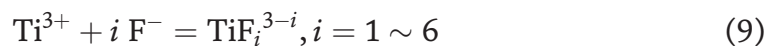
Relationship between r_i and apparent equilibrium constant of reaction (4) and (5) in NaCl-KCl molten salt at 1023 K (reprinted from Ref. [18]).

reactions (4) and (5) in NaCl-KCl molten salt under various content of fluoride [18]. It has been shown that the apparent equilibrium constants (K_{c1} and K_{c2}) for reactions (4) and (5) increased with the increasing of fluoride ion concentration in the molten salt. The equilibrium relationship between titanium ions and titanium metal is mainly present in the reaction (4) when the ratio of fluorine to titanium (r_i) is less than 1.8. Ti^{2+} was not detected in the molten salt with r_i greater than 1.8. Thus, the titanium ions in the molten salt were transferred, and it is present in reaction (5).

r_i is an important parameter to qualitatively investigate the equilibrium reactions among titanium ions. The initial concentration of titanium ions is also a factor that cannot be ignored. **Figure 4** is a graph showing the color change of samples under different r_i conditions at an initial concentration of Ti^{3+} of 4.6×10^{-3} (mol %). It can be seen that the color of the molten salt gradually changed from emerald green (color of Ti^{2+}) to the deep red (color of Ti^{3+}), and then gradually become shallower at various concentrations of fluoride ion.

The relationship between the initial concentration of Ti^{3+} , F^- and the concentration of the coordination compounds in the molten salt is shown in **Figure 5**. It can be seen that these three parameters are a smooth surface on the three-dimensional map. It indicates that the total concentration of the coordination compound is determined by the two parameters: initial concentration of Ti^{3+} and F^- .

The coordination reaction between fluoride ion and titanium ion (Ti^{3+}) is as shown in reaction (9):



The equilibrium constants of reaction (9) were evaluated using Eq. (10) [19]. **Table 2** shows the results of the best fitting of equilibrium constants for the complex formation.

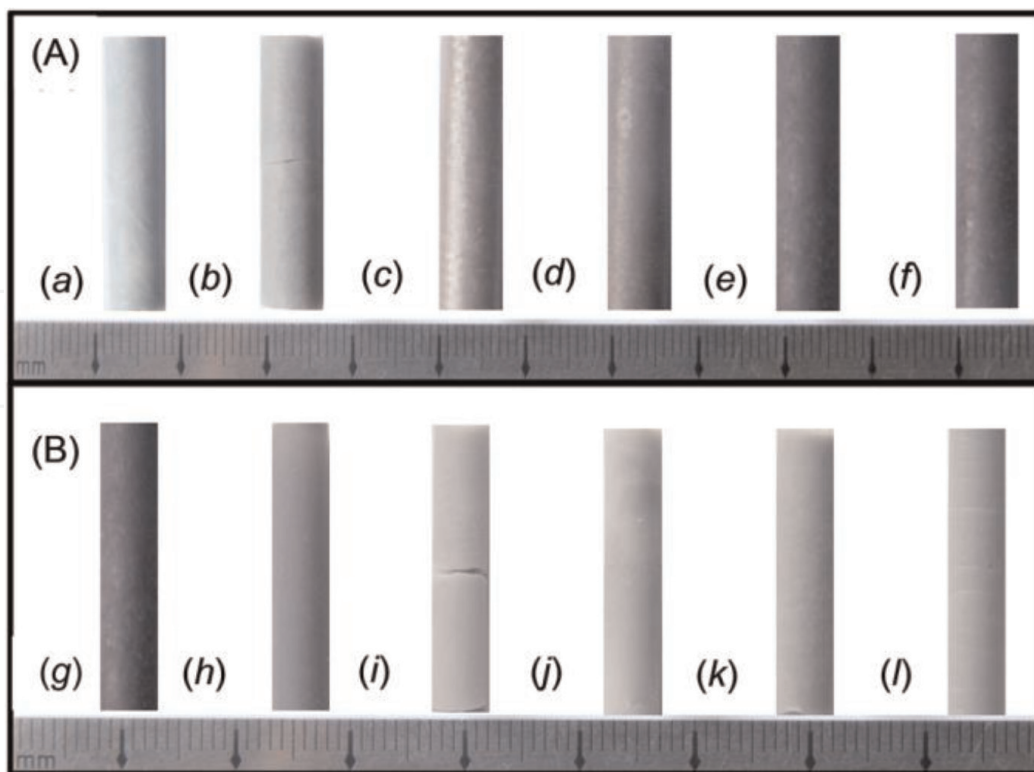


Figure 4. Samples of titanium chloride in the NaCl-KCl melt with different concentrations of fluoride at 1023 K. the initial concentration of Ti(III) was 0.46×10^{-2} and the concentration of fluoride, $x_{totalF^-}/10^{-2}$, was (A) region of a low fluoride content: (a) 0.0; (b) 2.6; (c) 5.3; (d) 6.4; (e) 7.7; (f) 9.0; (B) region of a higher fluoride content: (g) 10.0; (h) 10.5; (i) 11.4; (j) 12.1; (k) 13.0; and (l) 13.8 (reprinted from Ref. [19]).

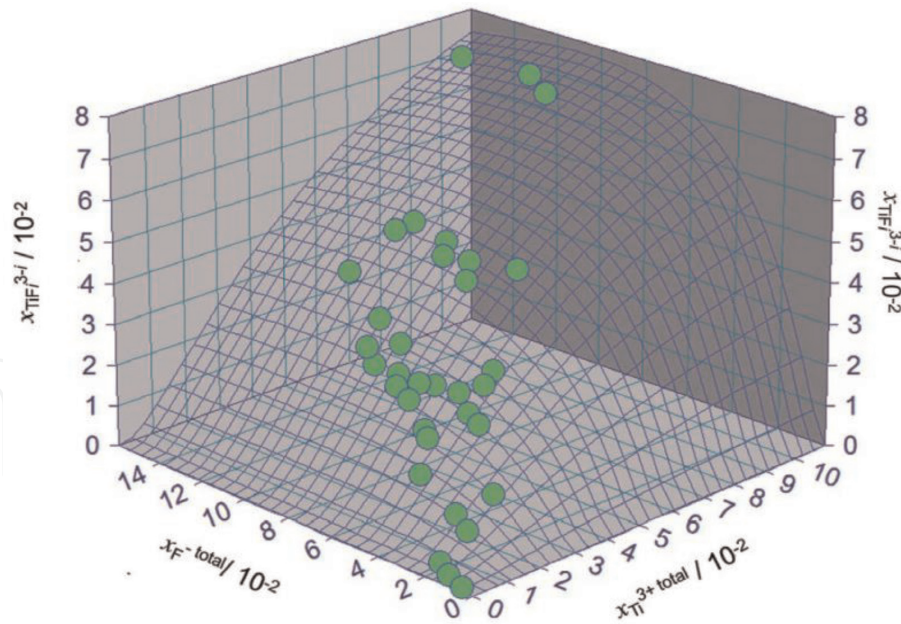


Figure 5.
The relationship between concentration of fluoride, Ti(III) and concentration of complexes at 1023 K (reprinted from Ref. [19]).

| TiF_i^{3-i} | K_i | $\Delta G_i^0/\text{kJ mol}^{-1}$ | $\Delta G_i^0 i^{-1}/\text{kJ mol}^{-1}$ |
|----------------------|----------------------|-----------------------------------|--|
| $i = 1$ | 3.9 | -11.6 | -11.6 |
| $i = 2$ | 3.5×10^2 | -49.8 | -24.9 |
| $i = 3$ | 4.5×10^{-5} | 85.2 | 28.4 |
| $i = 4$ | 4.1×10^4 | -90.4 | -22.6 |
| $i = 5$ | 1.6×10^{-8} | 133.1 | 26.6 |
| $i = 6$ | 5.8×10^6 | -132.4 | -22.1 |

Table 2.
The formation equilibrium constant and Gibbs free energies of complexes formation (reprinted from Ref. [19]).

$$K_i = \frac{a_{\text{TiF}_i^{3-i}}}{(a_{\text{F}^-}^{\text{eq.}})^i a_{\text{Ti}^{3+}}^{\text{eq.}}} = \frac{x_{\text{TiF}_i^{3-i}}}{(x_{\text{F}^-}^{\text{eq.}})^i x_{\text{Ti}^{3+}}^{\text{eq.}}}, i = 1 \sim 6 \quad (10)$$

Thus, it was found that the formation equilibrium constants of the complexes, TiF_i^{3-i} ($i = 1 \sim 6$), can be revalued by the best-fitting method. They are 3.9, 3.5×10^2 , 4.5×10^{-5} , 4.1×10^4 , 1.6×10^{-8} , and 5.8×10^6 , respectively. Using the equilibrium constants, the Gibbs free energies for the complex formation were revealed by Eq. (11):

$$\Delta G_i^0 = -RT \ln(K_i) \quad (i = 1 \sim 6) \quad (11)$$

where R is the gas constant and T is the absolute temperature. The results of the Gibbs free energies for the complex formation reactions are also shown in **Table 2**. It can be seen that the values of ΔG_1^0 , ΔG_2^0 , ΔG_4^0 , and ΔG_6^0 are negative, while ΔG_3^0 and ΔG_5^0 is positive. This corresponds to the extremely small value of K_3 and K_5 . It is well understandable in the coordination theory that the way of asymmetric coordination is uncommon. The real coordination number of anion (Cl^- , F^-) around each Ti(III) is 6, i is the number of F^- ion replaced the position of Cl^- .

In the complex with 3 and 5 F^- , one of F^- is coordinated in the opposite position of Cl^- . This asymmetric structure will cause relatively higher chemical potential than a symmetric structure. Therefore, the mainly existential states of the complexes are TiF_2^+ , TiF_4^- , and TiF_6^{3-} in NaCl-KCl melt when fluoride ions were added. The value of $\Delta G_i^0/i$ is also shown in **Table 2**. This value corresponds to the change of the Gibbs free energies for the reactions of each F^- replacing the position of Cl^- . As can be found from the table, the values are very close to each other, for TiF_2^+ , TiF_4^- , and TiF_6^{3-} , which is reasonable because they are all in symmetric coordination.

3.2.2 Effect of fluoride ion on reduction steps of titanium ions

The chemical behavior of fluoride ion and titanium ion in electrochemical process was examined by chemical method, respectively. The influencing mechanism of fluoride ion on the redox process of titanium ion was determined by various electrochemical analysis methods [20]. Under the condition of fluoride free in molten salt, cyclic voltammetry scanning results show that the Ti^{3+} reduction process was proceeded two-step, and they are below: $Ti^{3+} \rightarrow Ti^{2+}$ and $Ti^{2+} \rightarrow Ti$, respectively. However, when r_i was equals to 3.0, the reduction of Ti^{3+} was achieved by one step of $Ti^{3+} \rightarrow Ti$. Under such conditions, the power loss caused by the disproportionation reaction (4) can be effectively reduced.

The above studies show that fluoride ions can form coordination compounds with titanium ions to change the micro-structure of the molten salt, affect the equilibrium movement and electrochemical reduction steps of titanium ions in molten salt.

3.3 Influence of oxygen ions on ionic equilibrium of titanium

3.3.1 The formation of TiOCl in molten salt

Normally, the equilibrium constants of the disproportionation reactions were determined by concentration analyzing. However, the obtained equilibrium constant value (K_{c1}) for reaction (4) is severely dissipated, as shown in **Figure 6**.

The volatility of the K_{c1} value in molten salt that evaluated by the HCl treated is relatively small. Sekimoto [21] and other studies have shown that this is due to the coordination reaction (12) between Ti^{3+} and O^{2-} in the molten salt. The removal of oxygen from the molten salt by HCl will eliminate the effect of TiOCl on the concentration determination to some extent.



Based on above research, the influence of oxygen ions on the evaluation of the equilibrium constant of disproportionation reaction was considered, and the equilibrium constant value of reaction (4), the solubility product (K_{sp}) of TiOCl were estimated by the best-fitting method. More importantly, it provides a reliable method for evaluating the equilibrium constant of the disproportionation reaction. By using this method, a systematically study was carried out to investigate the influence of cation of electrolyte on the equilibrium constant [14, 23].

Considering the electrochemical behavior of Ti-O ions, Barner speculated that the intervention of oxygen ions makes the electrochemical reduction process similar to the homogeneous reaction due to the presence of the coordination compounds TiF_6^{2-} and $TiOF_5^{3-}$ [24].

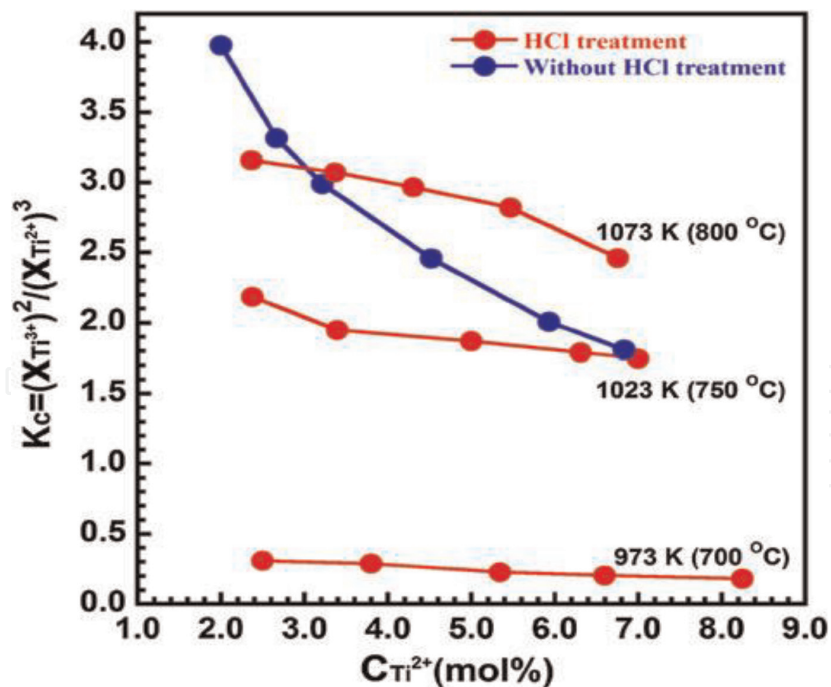


Figure 6.

Experiment data of K_c and $C_{Ti^{2+}}$ in NaCl-KCl equimolar melt at 973, 1023, and 1073 K, respectively (reprinted from Ref. [22]).

The above studies have shown that the formation of a coordination compound between oxygen ions and high-valent titanium ions in the molten salt brings about a deviation in the evaluation of the concentration of titanium ions. At the same time, Ti-O coordination compounds also affect the electrochemical reduction process of titanium ions.

3.3.2 Purification and quantification of oxide content

Oxygen ions are very sensitive elements in the high-purity titanium electrolytic refining process, so it is necessary to find a simple and accurate method for their quantitative analysis [25–27]. The determination of oxygen ions in the molten salt can also be achieved by electrochemical titration with YSZE (yttria-stabilized zirconia electrode). Castrilejo et al. discussed the concentration changes of oxygen ion in $CaCl_2$ -NaCl molten salt [28]. In addition, the square wave voltammetry was used to determine the relationship between current density and oxygen content in LiF-NaF-KF and LiF-NaF molten salts by Shen et al. [29] and Massot et al. [30], respectively. Thereby, three options for determining the oxygen content in molten salts can be concluded, namely: the best-fitting method, electrochemical titration technique (ETT), and square wave voltammetry (SWV).

Taking ETT as an example, in order to clarify the behavior of the impurity element (oxide) in molten salt, the electrochemical behavior of oxide ions has been investigated in an equimolar NaCl-KCl by electrochemical titration technique. The residual content of oxide in the molten NaCl-KCl was determined by using this in-situ method. The titrations of O^{2-} were applied by sodium oxide additions. The results obtained through electrochemical titration technique show that the oxide content in the melt and the free oxide ions (O^{2-}) detected content have a good linear relationship (Figure 7).

The equation of the fitted line is:

$$I_p = 5.71 \times 10^{-5} + 4.56 \times 10^{-6} x_{O^{2-}} \quad (13)$$

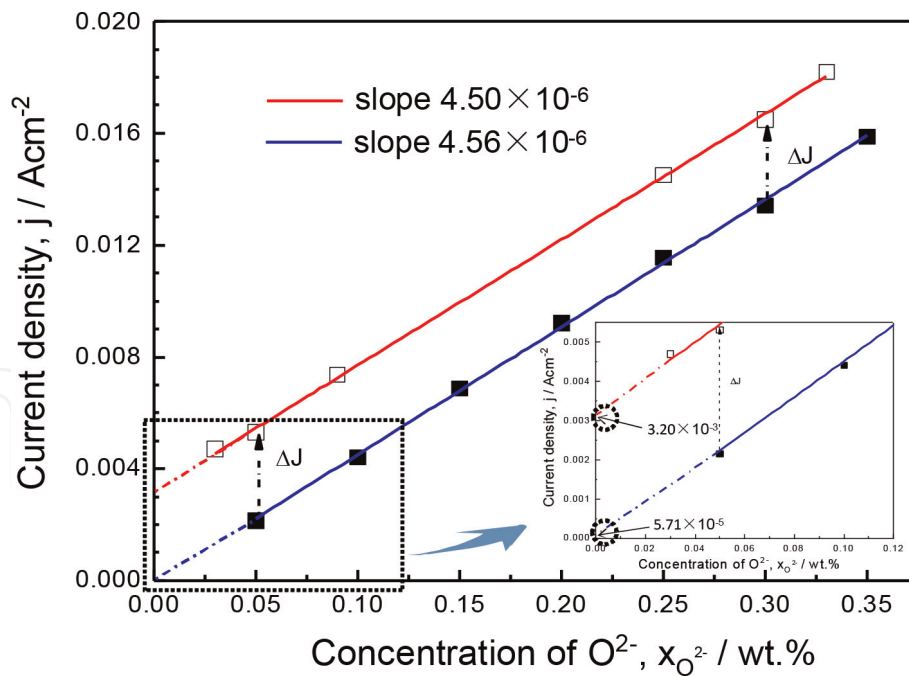


Figure 7.
 Linear relationship of the peak current density versus oxide ion content before and after purified with HCl (reprinted from Ref. [27]).

The value difference of slope can be explained as: the influence of O^{2-} decreased when its total concentration was on a high level. The line almost goes through the origin of the coordinates (the intercept equals to 5.71×10^{-5}), which means hardly any O^{2-} oxidation current can be detected with extremely low O^{2-} concentration dissolution in the NaCl-KCl melts. The current density differences (ΔJ) at a same concentration of O^{2-} are 0.0029 and 0.0027 Acm^{-2} , respectively. Thus, the residual concentration of O^{2-} can be estimated when plugging ΔJ into the Eq. (13), and the average value is 688 ppm.

3.4 Electro-refining of high-purity titanium in molten salt

3.4.1 Anodic polarization behavior in different molten salt structures

Oxidation occurs on the anode during electrolysis, and the anode material enters the molten salt in the form of ions. The electrochemical dissolution behavior is related to the electrolysis voltage, electrolyte composition, etc. [8, 31, 32]. Haarberg et al. investigated the electrochemical behavior of TiC_xO_y in NaCl-KCl and TiO_2 in Na_3AlF_6 molten salt. In the chloride molten salt, titanium ions are mainly dissolved in the form of Ti^{2+} , and the electrochemical precipitation of titanium ions is in the form of Ti^{3+} or Ti^{4+} in the molten salt of Na_3AlF_6 .

It is of great significance for optimizing molten salt electrolyte and improving electrolysis efficiency. Thus, the changes of micro-element structure in molten salt, and the influence of electrochemical dissolution and deposition of titanium ions should be clarified.

3.4.2 Electrochemical parameters for high-purity titanium extraction

The reason for the low efficiency in electrolysis process is that, power consumption caused by the coordination of titanium ions and anions in the molten salt. The physical and chemical properties of the molten salt relate to the basis of electrolysis electrode process in molten salt. Thereby, the current efficiency of high-purity

titanium electro-refining is related to the current density and the stable state of titanium ion in the molten salt. Concentrations of titanium ions and other parameters are also related [33–35]. Therefore, in order to achieve high-purity titanium with high-efficiency, the molten salt structure should be in-depth understood. It can be provided a guidance for improving the electrolysis efficiency and product quality.

4. Conclusions

Based on above analysis, comprehensive and systematic conclusions were done on the scientific issues to be clarified in the high-purity titanium molten salt electro-refining process. The influence of anion and cation in electrolyte on ionic equilibrium of titanium was discussed systematically by chemical analysis and electro-chemical testing. Specifically, the type of microstructure of the molten salt is dissected in the molten salt mainly composed of chloride. The coordination mechanism between titanium ion and fluoride ion was also revealed. The mechanism of anodic oxidation and cathodic reduction kinetics in electrolytes with different micro-structures was clarified, which provide a guiding line for optimizing electrolyte. More importantly, on the basis of full theoretical and experimental research, it proposes parameters for high-purity titanium extraction in molten salt, and provides theoretical support for the establishment of efficient, low-pollution, and low-cost metallurgical processes.

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