The Equilibrium Between Titanium Ions and Titanium Metal in NaCl-KCl Equimolar Molten Salt

QIUYU WANG, JIANXUN SONG, GUOJING HU, XIAOBO ZHU, JUNGANG HOU,
SHUQIANG JIAO, and HONGMIN ZHU

The equilibrium between metallic titanium and titanium ions, $3Ti^{2+} \rightleftharpoons 2Ti^{3+} + Ti$, in NaCl-KCl equimolar molten salt was reevaluated. At a fixed temperature and an initial concentration of titanium chloride, the equilibrium was achieved by adding an excess amount of sponge titanium in assistant with bubbling of argon into the molten salt. The significance of this work is that the accurate concentrations of titanium ions have been obtained based on a reliable approach for taking samples. Furthermore, the equilibrium constant $K_C = (x^{eql}_{Ti^{3+}})^3/(x^{eql}_{Ti^{2+}})^2$ was calculated through the best-fitting method under the consideration of the TiOCl dissolution. Indeed, the final results have disclosed that the stable value of K_C could be achieved based on all modifications.

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I. INTRODUCTION

TITANIUM, the ninth most abundant element in the Earth's crust, is endowed with high strength, low density, excellent flexibility, strong spring-back characteristics, high-temperature performance, corrosion resistance, and biocompatibility. These characteristics make titanium eminently suitable to be used in aerospace, marine industries, and harsh chemical environments. Although it has many excellent properties, the application of titanium in industry is limited by its high cost. Therefore, many methods have been investigated for producing titanium metal at a low cost. Recently, electrolysis with the starting materials of titanium oxides was considered as a promising method for titanium metallurgy, such as the FFC-Cambridge process,[1,2] the OS process,[3–6] the molten oxide electrolysis (MOE),[7] and the electrolysis of titanium oxycarbides (the USTB[8–10] and the MER[11] processes). In the USTB process, when titanium oxycarbide was used as the anode in a molten salt bath, carbon monoxide was evolved, with titanium leaving the anode as titanium ions and diffusing to the cathode before being deposited to form titanium with low oxygen content.[8–10] However, titanium ions dissolved from oxycarbide anode could be present in the electrolyte with various valences that may favor reoxidation and disproportionation reactions, resulting in a low current density.

Actually, many works have examined the investigation of electrochemical behavior of titanium ions in molten chloride, fluoride, and chloride-fluoride electrolytes.[12–20] The published literature has disclosed that a two-step process of $Ti^{3+} \rightarrow Ti^{2+} \rightarrow Ti$ was generally taking place in chloride melts.[13] In comparison, Ti^{3+} was directly reduced to be titanium in fluoride melts.[17] With the starting activation material of Ti^{4+}, it proceeded as a two-step process: $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti$ in chlorides or as a three-step process: $Ti^{4+} \rightarrow Ti^{3+} \rightarrow Ti^{2+} \rightarrow Ti$ in fluorides, respectively.[18–20] Indeed, the stability of the titanium ions depends on the bath composition.[21] The Ti^{2+} was more stable in alkali chloride melts, and correspondingly, in alkali fluoride melts, the higher oxidation states of Ti^{4+} and Ti^{3+} were more stable.

It has been reported that equilibrium exists among Ti^{2+}, Ti^{3+}, and metallic titanium in most chloride melts, which can be expressed by Reaction [1]:

$$3Ti^{2+} \rightleftharpoons 2Ti^{3+} + Ti \qquad [1]$$

The equilibrium constant K_C is defined by Eq. [2]:

$$K_C = \frac{x^2_{Ti^{3+}} x_{Ti}}{x^3_{Ti^{2+}}} = \frac{x^2_{Ti^{3+}}}{x^3_{Ti^{2+}}} \qquad [2]$$

In molten salts, the activity of pure Ti is considered to be unity, where $x_i$is the cationic molar fraction of a species i and is defined by the following Eq. [3]:

$$x_i = \frac{100 n_i}{n_{Na^+} + n_{K^+} + n_{Ti^{2+}} + n_{Ti^{3+}}} \qquad [3]$$

In previous works,[22–30] to obtain the equilibrium constant K_C, the concentrations of Ti^{2+} and Ti^{3+} were determined by the H_2 volumetric analysis and titration. The H_2 volumetric analysis was based on the fact that $TiCl_2$ could react with hydrochloric acid solution and H_2 gas evolution as follows in Reaction [4]:

QIUYU WANG, JIANXUN SONG, GUOJING HU, and XIAOBO ZHU, Students, and JUNGANG HOU, SHUQIANG JIAO, and HONGMIN ZHU, Professors, are with the State Key Laboratory of Advanced Metallurgy, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China. Contact e-mail: hzhu@metall.ustb.edu.cn

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$$2\mathrm{TiCl_2} + 2\mathrm{HCl} \rightarrow 2\mathrm{TiCl_3} + \mathrm{H_2}\uparrow \qquad [4]$$

The concentration of $\mathrm{Ti^{3+}}$ in the solution was determined by the titration by the Reaction [5]:

$$\mathrm{Ti^{3+}} + \mathrm{Fe^{3+}} \rightarrow \mathrm{Ti^{4+}} + \mathrm{Fe^{2+}} \qquad [5]$$

In general, $\mathrm{K_C} = (x^{\mathrm{anal}}_{\mathrm{Ti^{3+}}})^2/(x^{\mathrm{anal}}_{\mathrm{Ti^{2+}}})^3$ should be a constant as the solutes ($\mathrm{TiCl_3}$, $\mathrm{TiCl_2}$) obey Henry's law under the condition of low titanium ions concentration. However, publications in the literature have reported that $\mathrm{K_C}$ depended on the total titanium concentration.[24–26] Mellgren and Opie pointed out that the divalent and trivalent Ti were associated into $(\mathrm{TiCl_2})_3$ and $(\mathrm{TiCl_3})_2$ resulted in the constant $\mathrm{K_C}$ values for the reaction $(\mathrm{TiCl_3})_2 + \mathrm{Ti} = (\mathrm{TiCl_2})_3$.[24] Kreye and Kellogg reported that the Temkin's rule for the ideal behavior of ionic melts was applied to the equilibrium results.[25] The reported $\mathrm{K_C}$ values were significantly related to the titanium ion concentration, which implied that it was not easy to obtain the real concentration of titanium ions in the melts. Normally, the concentration of $\mathrm{TiCl_2}$ could be underestimated through the $\mathrm{H_2}$ evolution method due to the formation of titanium hydrides or titanium hydrogen solid solution.[27,28] On the other hand, $\mathrm{Ti^{3+}}$ could react with $\mathrm{O^{2-}}$ and $\mathrm{Cl^-}$ to form titanium oxychloride TiOCl(s) and cause overestimation of $\mathrm{Ti^{3+}}$ in the chemical analysis. Sekimoto *et al.* investigated the $\mathrm{K_C}$ of the equilibrium between titanium ions and Ti and considered the possible error. The equilibrium constant $\mathrm{K_C}$ was reevaluated by consideration the $\mathrm{K_{SP}}$ of the reaction: $\mathrm{TiOCl(s)} \rightleftharpoons \mathrm{Ti^{3+}} + \mathrm{Cl^-} + \mathrm{O^{2-}}$.[29,30] However, the $\mathrm{K_C}$ was still dispersing especially in low titanium ion concentration.

In this work, the accurate concentrations of titanium ions were obtained based on a reliable approach for taking samples, which was found *via* the comparison of different routes using the chemical analysis. The $\mathrm{K_C}$ and $\mathrm{K_{SP}}$ were obtained in NaCl-KCl equimolar molten salt at 973 K, 1023 K, and 1073 K (700 °C, 750 °C, and 800 °C), respectively.

II. EXPERIMENT

A. *Preparation of Samples*

The titanium dichloride was prepared through $\mathrm{TiCl_4}$ gas reacting with an excess amount of metallic titanium in NaCl-KCl (reagent grade; Beijing Chemical Industries, Beijing, P.R. China) equimolar molten salt.[15] The solvent salts were prepared by the following procedure. The equimolar mixture of NaCl-KCl equimolar molten salt was dried at 623 K (350 °C) in a vacuum for 24 hours. Subsequently, the mixture was heated up to melt at 1023 K (750 °C) in a high-purity argon atmosphere (99.999 pct). Additionally, high-purity hydrogen chloride gas (99.999 pct) was bubbled into the salt to remove the $\mathrm{O^{2-}}$. Temperature control within ±2 °C was achieved with a digital temperature controller (CHINO DZ3000; CHINO Corporation, Tokyo, Japan) and measured using a K-type thermocouple (Omega Engineering, Inc., Stamford, CT). The premelted salts were cooled under the high-purity argon atmosphere and then transferred into the glove box, where the content of water and oxygen was maintained under 0.2 ppm. The oxygen ion concentration in the solvent salts was measured by a nitrogen/oxygen analyzer (TC500-Series; LECO Corporation, St. Joseph, MI).

Figure 1(a) shows an experimental apparatus for equilibrium between the titanium ions and titanium metal. The salts containing titanium dichloride and excess metallic titanium were held at a designed temperature to reach equilibrium. High-purity argon gas was used to stir the molten salts for making the reaction of titanium ions and titanium metal fast. Figure 1(b) shows a schematic diagram of the quartz sampler. The quartz sampler consists of an injector and a quartz tube. The injector at the top of the quartz tube (6 mm diameter) is sealed by a rubber plug. Four parallel samples were taken out from molten salts by the quartz sampler for analysis in each experiment, and the average value of the concentrations of titanium ions was considered as the result.

B. *Analysis for Titanium Ions*

The concentrations of $\mathrm{Ti^{2+}}$ and $\mathrm{Ti^{3+}}$ in the sample were determined by $\mathrm{H_2}$ volumetric analysis, titration, and spectrophotometry, respectively. First, the concentration of $\mathrm{Ti^{2+}}$ was quantitated by $\mathrm{H_2}$ volumetric analysis as follows in Reaction [6]:

$$2\mathrm{TiCl_2} + 2\mathrm{HCl} \rightarrow 2\mathrm{TiCl_3} + \mathrm{H_2}\uparrow \qquad [6]$$

The concentration of $\mathrm{Ti^{2+}}$ was calculated by measuring the hydrogen volume. The oxygen dissolved in diluted hydrochloric acid has strong oxidization, so that it may oxidize $\mathrm{Ti^{2+}}$ and underestimate the concentration of $\mathrm{Ti^{2+}}$ in the sample. Hence, the $\mathrm{O_2}$ dissolved in deionized water was removed by the method of vacuum degassing. High-purity argon was bubbled through the deionized water for 30 minutes in order to prevent the $\mathrm{O_2}$ dissolve in the water. The above steps were cycled about three times. After that, the deoxygenized water was obtained. A certain amount of concentrated hydrochloric acid was injected into the deoxygenized water to prepare diluted hydrochloric acid (1.0 mol/L). The deoxygenized hydrochloric acid solution was saturated by bubbling high-purity $\mathrm{H_2}$ for more than 30 minutes in order to prevent the $\mathrm{H_2}$ evolved by the Reaction [6] from dissolving in the hydrochloric acid solution.

The concentration of $\mathrm{Ti^{3+}}$ in the solution consists of two parts, that is, initial trivalent titanium ion in the sample and the oxidized $\mathrm{Ti^{3+}}$ from Reaction [6]. The total concentration of $\mathrm{Ti^{3+}}$ in the solution was determined by the titration using 0.05M $\mathrm{NH_4Fe(SO_4)_2}$ aqueous solution. The $\mathrm{Ti^{3+}}$ in the solution reacts with $\mathrm{Fe^{3+}}$ by Reaction [7]:

$$\mathrm{Ti^{3+}} + \mathrm{Fe^{3+}} \rightarrow \mathrm{Ti^{4+}} + \mathrm{Fe^{2+}} \qquad [7]$$

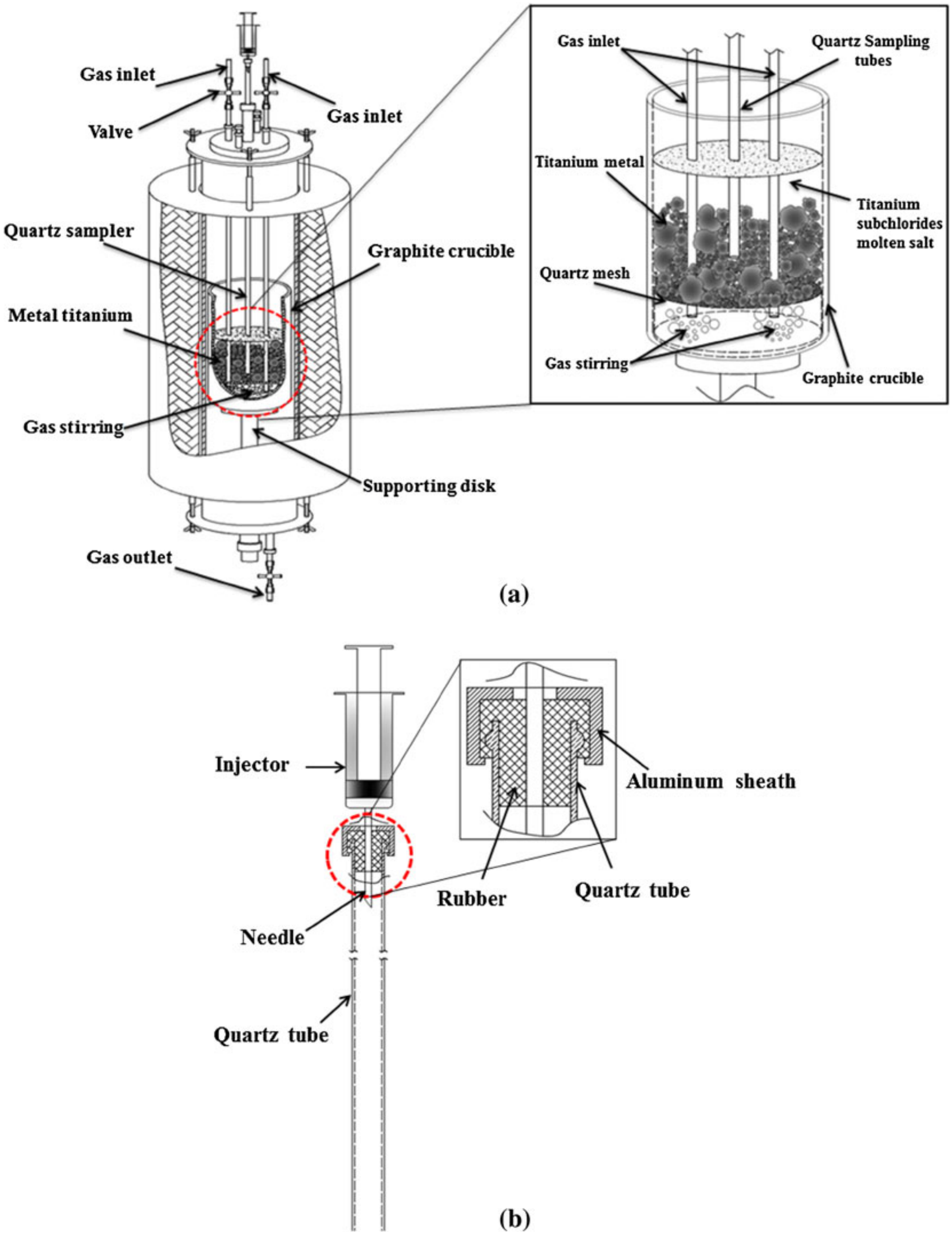


Fig. 1—(*a*) Experimental setup: schematic diagram of equilibration apparatus and (*b*) quartz sampler.

Finally, that the concentration of Ti^{4+} from Reaction [7] was equal to the concentration of Ti^{2+} plus Ti^{3+} was determined by diantipyryl methane spectrophotometry.[31]

III. RESULTS AND DISCUSSION

Both the solvent salts with and without removing the O^{2-} were measured by a nitrogen/oxygen analyzer. The O^{2-} content in the molten salt depends on the way of the pretreatment. The concentration of O^{2-} was decreased from initial concentration of about 1600 ppm, to about 800 ppm and 200 ppm with the pretreatment by vacuum drying and hydrochloric acid treatment, respectively.

Figure 2 shows the three ways of taking the sample from the molten salt at 1023 K (750 °C). Figure 2(a) shows the way of taking the sample from the molten salt without filtering. It was found that a large amount of titanium powder dispersed in the sample. Four parallel samples were taken from the molten salts for a chemical analysis, and the results are shown in Table I. The

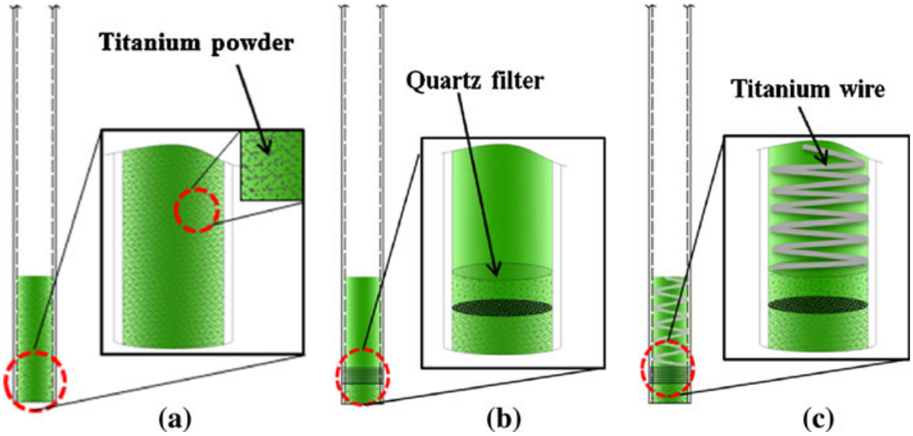


Fig. 2—Schematic diagrams of three methods of sampling: (*a*) the sample containing the dispersed Ti powder without filtering, (*b*) the sample with filtering the titanium powder, and (*c*) the sample with filtering the titanium powder and a titanium wire for keeping the equilibrium.

Table I. Chemical Analysis Results of Ti Powder, $x^{\text{anal}}_{\text{Ti}^{2+}}$, $x^{\text{anal}}_{\text{Ti}^{3+}}$, and K_C

Sample	Dispersed Ti Powder (Weight Percent)	$x^{\text{anal}}_{\text{Ti}^{2+}} \times 10^2$	$x^{\text{anal}}_{\text{Ti}^{3+}} \times 10^2$	K_C	Relative Standard Deviation (Pct)
1	0.52	6.77	1.58	0.80	83.91
2	1.21	7.35	1.27	0.41	
3	1.79	7.79	0.88	0.16	
4	2.10	8.07	0.80	0.12	

Table II. Chemical Analysis Results of $x^{\text{anal}}_{\text{Ti}^{2+}}$, $x^{\text{anal}}_{\text{Ti}^{3+}}$, and K_C After Filtering the Titanium Powder

Sample	$x^{\text{anal}}_{\text{Ti}^{2+}}$ ($\times$ 10^2)	$x^{\text{anal}}_{\text{Ti}^{3+}}$ ($\times$ 10^2)	K_C	Relative Standard Deviation (Pct)
1	5.79	2.35	2.84	21.74
2	5.98	2.23	2.32	
3	6.16	2.08	1.85	
4	6.18	2.07	1.82	

Table III. Chemical Analysis Results of $x^{\text{anal}}_{\text{Ti}^{2+}}$, $x^{\text{anal}}_{\text{Ti}^{3+}}$, and K_C with Filtering and a Titanium Wire for Keeping the Equilibrium

Sample	$x^{\text{anal}}_{\text{Ti}^{2+}}$ ($\times$ 10^2)	$x^{\text{anal}}_{\text{Ti}^{3+}}$ ($\times$ 10^2)	K_C	Relative Standard Deviation (Pct)
1	6.15	2.00	1.72	1.50
2	6.14	1.99	1.71	
3	6.23	2.02	1.69	
4	6.25	2.03	1.69	

chemical analysis result shows that the concentrations of Ti^{2+} and Ti^{3+} depended on the mass of titanium powder. Meanwhile, the concentration of Ti^{2+} increased with increasing the mass of titanium powder, similar with the tendency reported by Komarek *et al.*[27] experimentally. It is indicated that the titanium powder might react with hydrochloric acid and evolves H_2 gas. The dispersed Ti generated from the disproportionation Reaction [1] is in the molten salts. Because the surface of dispersed Ti is fresh and not covered by a passivation film, it can react with hydrochloric acid solution. In order to prove this hypothesis, another sample was set up.

Figure 2(b) shows the method with filtering dispersed titanium, and the chemical analysis of titanium ions is shown in Table II. The results show that the concentrations of Ti^{2+} and Ti^{3+} are more stable than those without filtering the dispersed titanium. The concentrations of Ti^{2+} and Ti^{3+} are relatively stable but still volatile, and the relative standard deviation of K_C is 16.9 pct. Meanwhile, the concentration of Ti^{3+} generally increased with the decrease of the concentration of Ti^{2+}. It indicates that this tendency might be caused by the disproportion reaction of TiCl_2, $\text{TiCl}_2 \rightarrow 2\text{TiCl}_3 + \text{Ti}$, and the equilibrium reaction is broken by removing the dispersed titanium. In order to prove this hypothesis, another way of sampling was set up as shown in Figure 2(c). A titanium wire can keep the equilibrium after filtering dispersed titanium. The chemical analysis results of sample are shown in Table III. The results show that the concentrations of Ti^{2+} and Ti^{3+} are very stable

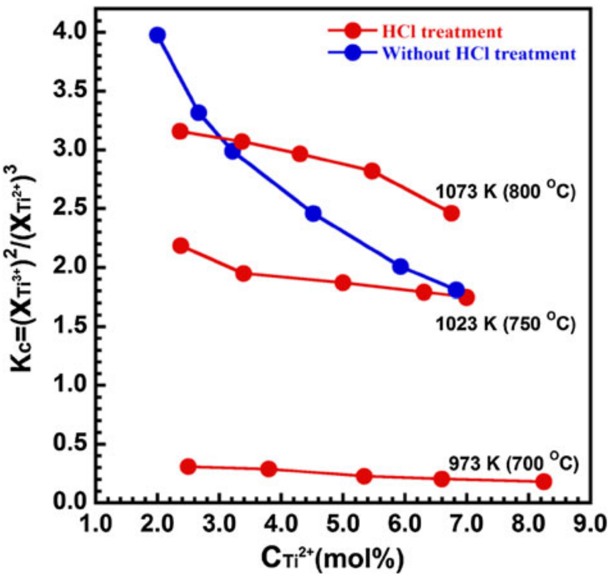
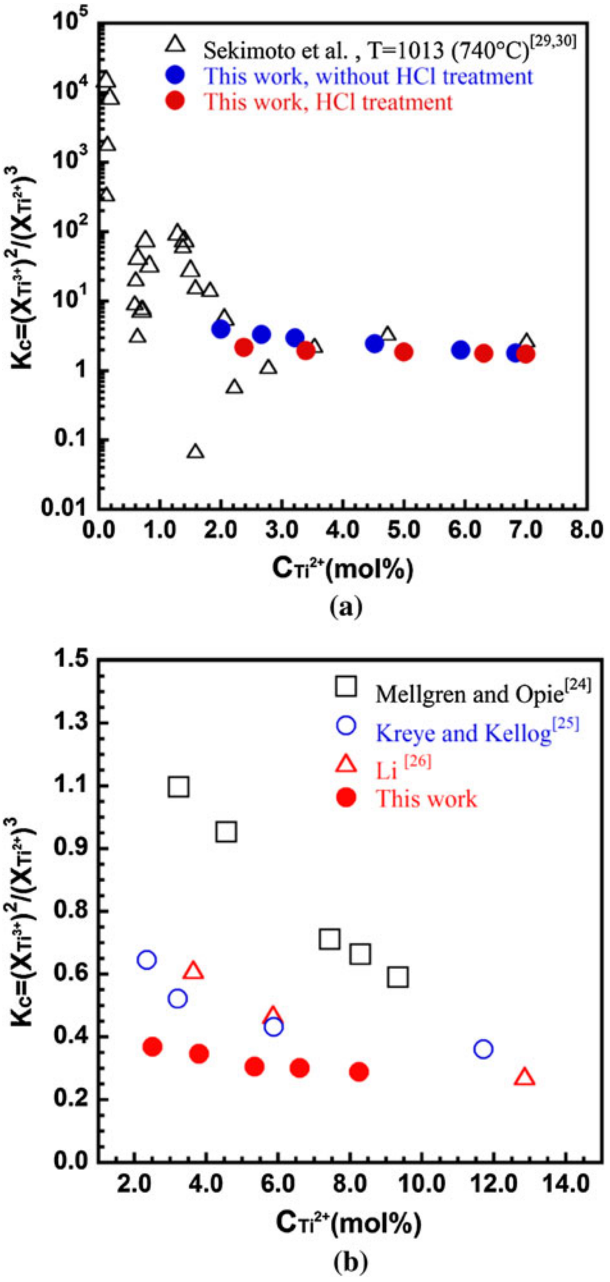


Fig. 3—Experiment data of K_C and $C_{Ti}{}^{2+}$ in NaCl-KCl equimolar melt at 973 K, 1023 K, and 1073 K (700 °C, 750 °C, and 800 °C), respectively.

and the relative standard deviation of K_C is 1.50 pct. Based on all the analysis mentioned above, it was obtained the best way for sampling that Ti powder is filtered and a titanium wire inserted in a quartz tube for keeping the equilibrium.

This best way of taking the sample was used in this work. The equilibrium constant K_C was obtained in a NaCl-KCl equimolar molten salt with different titanium ion concentrations and temperatures. Figure 3 shows the relationship between K_C and $C_{Ti}{}^{2+}$ at 973 K, 1023 K, and 1073 K (700 °C, 750 °C, and 800 °C) of this work. It was found that the equilibrium constant K_C increases with the increase in temperature. In the meantime, K_C decreases with an increase in the concentration of Ti^{2+} at a fixed temperature. The equilibrium constant K_C of the molten salts without hydrogen chloride treatment is greater than that with hydrogen chloride treatment at 1023 K (750 °C).

Figure 4(a) shows the relationship between K_C and $C_{Ti}{}^{2+}$ at 1023 K (750 °C) compared with the literature. The equilibrium constant K_C in this study is more stable than that reported by Sekimoto *et al*.[29,30] Figure 4(b) shows the relationship between K_C and $C_{Ti}{}^{2+}$ at 975 K (700 °C) compared with the literature. The results of this study are close to that found in the literature[24–26] and are more stable. The equilibrium constant K_C depends weakly on the concentration of Ti^{2+} in this work. The literature showed the same tendency that the value of K_C depends on the titanium ion concentration. In general, K_C should be a constant because the solutes ($TiCl_2$, $TiCl_3$) obey Henry's law when the total titanium ion concentration is low. The reason of this trend may be caused by the influence of O^{2-} in the molten salt. The initial oxide ions O^{2-}, Ti^{3+}, and Cl^- form insoluble TiClO(s) deposition, leading to an overestimate of the Ti^{3+} concentration. Therefore, the equilibrium constant K_C is dispersed. The equilibrium constant K_C is monotonically decreasing and becoming stable with increasing the concentration of Ti^{2+}. The influence of O^{2-} on the K_C reduces with the increase of the total titanium concentration because the content of initial oxide ion O^{2-} in a molten salt is constant. In order to obtain an accurate K_C, the influence of O^{2-} should be taken into account.



(a)

(b)

Fig. 4—Relationship between K_C and $C_{Ti}{}^{2+}$ of experiment data compared with the literature (*a*) at 1023 K (750 °C) and (*b*) at 973 K (700 °C). The open symbols and filled symbols correspond to the reported and measured values in this study, respectively.

The best-fitting method is used for analyzing the experimental data of this work. The equilibrium constant K_C monotonically decreases with the concentration of Ti^{2+} increased at 973 K, 1023 K, and 1073 K (700 °C, 750 °C, and 800 °C) in this work. Meanwhile, the solubility product K_{SP} of TiOCl(s), the equilibrium constant K_C, and the initial concentration O^{2-} are constant values in a certain molten salts at a fixed temperature. Based on the two conditions, the best-fitting equation is set up as follows.

The Ti^{3+} can react with O^{2-} and Cl^{-} to form TiOCl(s) and is expressed by the following reaction:

$$\mathrm{TiOCl(s)} \rightleftharpoons \mathrm{Ti^{3+}} + \mathrm{O^{2-}} + \mathrm{Cl^{-}} \qquad [8]$$

The solubility product of TiOCl(s), $K_{sp,}$ is defined by the following Eq. [9]:

$$K_{sp} = \frac{x_{Ti^{3+}} x_{O^{2-}} x_{Cl^{-}}}{x_{TiOCl(s)}} = x^{eql}_{Ti^{3+}} x^{eql}_{O^{2-}} \qquad [9]$$

In the equation, $x^{initial}_{O^{2-}}$ is the initial concentration of oxide ion in the molten salt. The activities of chloride ion and TiOCl(s) are considered to be unity in the molten salt. The relationships between the equilibrium concentrations of $x^{eql}_{Ti^{2+}}$ and $x^{eql}_{Ti^{3+}}$ are evaluated and expressed as follows:

$$x^{eql}_{Ti^{2+}} = x^{anal}_{Ti^{2+}} \qquad [10]$$

$$x^{anal}_{Ti^{3+}} = x^{eql}_{Ti^{3+}} + x^{eql}_{TiOCl(s)} \qquad [11]$$

The mass balance of oxide ion is represented by Eq. [12]:

$$x^{initial}_{O^{2-}} = x^{eql}_{O^{2-}} + x^{eql}_{TiOCl(s)} \qquad [12]$$

The term $x^{eql}_{Ti^{3+}}$ can be represented in Eq. [13], according to Eqs. [9] through [12].

$$x^{eql}_{Ti^{3+}} = \frac{\left(x^{anal}_{Ti^{3+}} - x^{initial}_{O^{2-}}\right) + \sqrt{\left(x^{initial}_{O^{2-}} - x^{anal}_{Ti^{3+}}\right)^2 + 4K_{sp}}}{2} \qquad [13]$$

According to Eqs. [2], [10] and [13], K_C can be revaluated and expressed as follows:

$$K_C = \frac{\left(x^{eql}_{Ti^{3+}}\right)^2}{\left(x^{eql}_{Ti^{2+}}\right)^3} = \frac{\left[\dfrac{\left(x^{anal}_{Ti^{3+}} - x^{initial}_{O^{2-}}\right) + \sqrt{\left(x^{initial}_{O^{2-}} - x^{anal}_{Ti^{3+}}\right)^2 + 4K_{sp}}}{2}\right]^2}{\left(x^{eql}_{Ti^{2}}\right)^3} \qquad [14]$$

According to Eq. [14], the best-fitting equation can be expressed as follows:

$$x^{eql}_{Ti^{2+}} = x^{anal}_{Ti^{2+}} = \left\{\frac{\left[\left(x^{anal}_{Ti^{3+}} - x^{initial}_{O^{2-}}\right) + \sqrt{\left(x^{initial}_{O^{2-}} - x^{anal}_{Ti^{3+}}\right)^2 + 4K_{sp}}\right]^2}{4K_C}\right\}^{\frac{1}{3}} \qquad [15]$$

The experimental data were expressed by the best-fitting method through the best-fitting Eq. [15]. The K_{SP}, K_C, and $x^{initial}_{O^{2-}}$ are calculated as the best-fitting parameters by fitting the experimental data $x^{anal}_{Ti^{2+}}$ and $x^{anal}_{Ti^{3+}}$. Figure 5 shows the relationship between the best-fitting curve and the experiment data at 1023 K (750 °C). The best-fitting curves correspond well with the experiment data. The calculated results of K_C, K_{SP}, and $x^{initial}_{O^{2-}}$ in ppm are shown in Table IV. It is observed that both the K_C and K_{SP} in the best-fitting parameters correspond well in NaCl-KCl equimolar solvent salts with a different method of treatment. Meanwhile, the value of $x^{initial}_{O^{2-}}$ is close to the chemical analysis result that the O^{2-} content in solvent salts about 800 ppm and 200 ppm with the pretreatment by vacuum drying and hydrochloric acid treatment, respectively. The reason is that, based on the Henry's law, the K_C and K_{SP} are constant values in a certain salt and fixed temperature in the region where the concentrations of titanium ions are low. On the other hand, the concentration of O^{2-} in the salt depends on the treament of the hydrogen chloride gas. The $x^{eql}_{Ti^{3+}}$ is calculated according to Eq. [13] using the best-fitting parameters of K_C, K_{SP}, and $x^{initial}_{O^{2-}}$. The K_C was reevaluated according to Eq. [14]. The relationship among the K_C of experiment data, the revaluation data and the best-fitting parameters are shown in Figure 6(a). All experiment data of K_C are revaluated back to a constant value equal to the best-fitting value. It indicates that K_C, K_{SP}, and $x^{initial}_{O^{2-}}$ were obtained from the accuracy parameters by the best-fitting method. It can be concluded that the value of K_C is around 1.55 at 1023 K (750 °C) in this solvent. Based on the above description, the equilibrium constant K_C was concluded by the best-fitting method in the same way even at 973 K and 1073 K (700 °C and 800 °C) as shown in Figure 6(a). All experiment data of K_C are revaluated back to a constant value that is equal to the best-fitting value. All the best-fitting parameters of K_C, K_{SP}, and $x^{initial}_{O^{2-}}$ are shown in Table V. It is observed that the best-

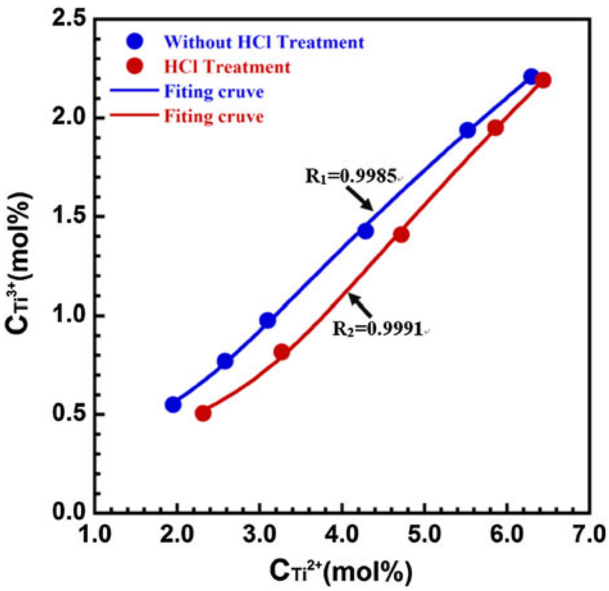


Fig. 5—Relationship between the best-fitting curve and the experiment data of $x^{anal}_{Ti^{2+}}$ and $x^{anal}_{Ti^{3+}}$ at 1023 K (750 °C).

Table IV. Best-Fitting Parameters of K_C, K_{SP}, and $x_{O^{2-}}^{initial}$ at 1023 K (750 °C)

Temperature [K (°C)]	Treatment of Molten Salt	K_C Fitting Value	$K_{SP} \times 10^5$ Fitting Value	$x_{O^{2-}}^{initial}$ (ppm) Fitting Value
1023 (750)	HCl treatment	1.52	2.02	153
1023 (750)	without HCl treatment	1.57	2.67	782

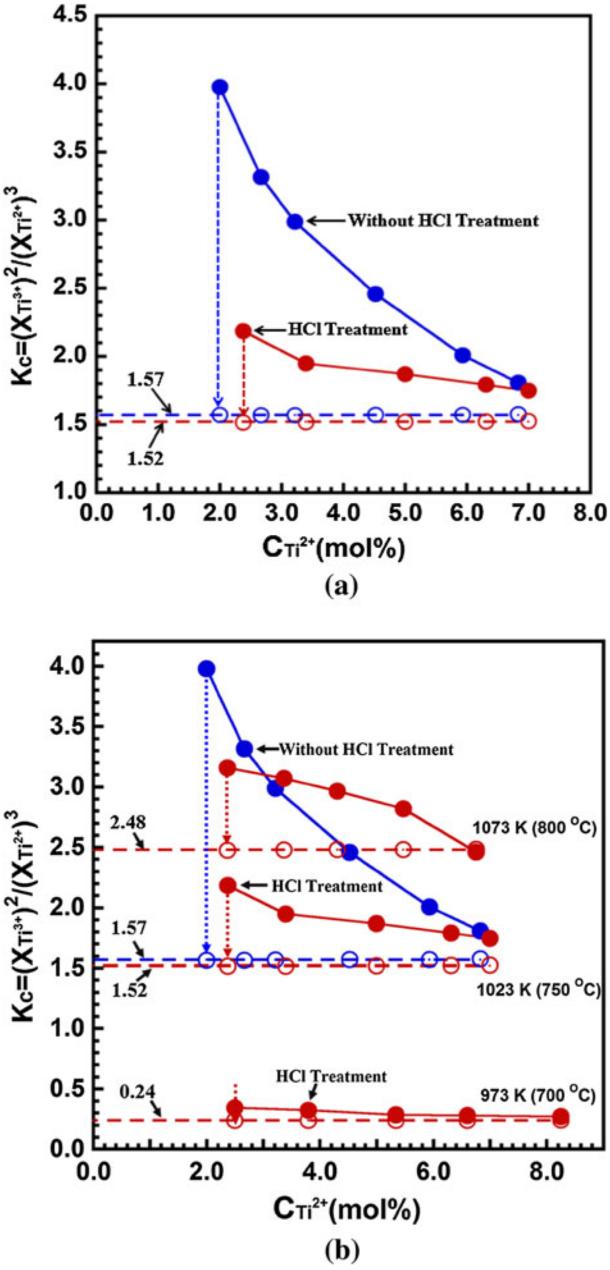


Fig. 6—Relationship between the equilibrium constant K_C of the experiment data, revaluated data, and best-fitting parameters (*a*) at 1023 K (750 °C), and (*b*) at 973 K, 1023 K, and 1073 K (700 °C, 750 °C, and 800 °C). The filled circle symbol, open circle symbol, and dotted line represent the experiment data, revaluation data, and best-fitting value, respectively.

Table V. Best-Fitting Parameters of K_C, K_{SP}, and $x_{O^{2-}}^{initial}$ at 973 K, 1023 K, and 1073 K (700 °C, 750 °C, and 800 °C), respectively

Temperature [K (°C)]	Treatment of Molten Salt	K_C Fitting Value	$K_{SP} \times 10^5$ Fitting Value	$x_{O^{2-}}^{initial}$ (ppm) Fitting Value
973 (700)	HCl treatment	0.24	1.29	175
1023 (750)	HCl treatment	1.52	2.02	153
1023 (750)	without HCl treatment	1.57	2.67	782
1073 (800)	HCl treatment	2.48	4.98	197

fitting parameters of initial $x_{O^{2-}}^{initial}$ are 153 to 197 ppm by hydrochloric acid treatment and 782 ppm by only vacuum drying without hydrochloric acid treatment, respectively. This result is close to the chemical analysis result indicating that the concentration of O^{2-} decreased from an initial concentration of about 1600 ppm to about 800 ppm and 200 ppm with the pretreatment by vacuum drying and hydrochloric acid treatment, respectively. The equilibrium constant K_C increased with the temperature increase. This result is close to the result previously reported.[26]

IV. CONCLUSIONS

The equilibrium among metallic titanium and titanium ions, $3Ti^{2+} \rightleftharpoons 2Ti^{3+} + Ti$, in NaCl-KCl equimolar molten salt was evaluated. The concentration of Ti^{2+} and Ti^{3+} could be overestimated by the titanium powder dispersed in sample and the initial contamination of O^{2-} in the solvent salt due to the TiClO(s) deposition, respectively. The equilibrium constant $K_C = (x_{Ti^{2+}})^3/(x_{Ti^{3+}})^2$ was calculated by the best-fitting method at 0.24 at 973 K (700 °C), 1.55 at 1023 K (750 °C), and 2.48 at 1073 K (800 °C), respectively. The equilibrium constant K_C increased with an increase in temperature.

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