# Revaluation of equilibrium quotient between titanium ions and metallic titanium in NaCl–KCl equimolar molten salt

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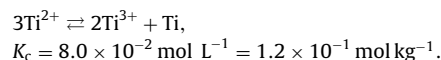
## ARTICLE INFO

## ABSTRACT

In this study, the effect of oxide ion on the equilibrium between titanium ions and metallic titanium was investigated in NaCl–KCl equimolar molten salt. The soluble species containing $Ti^{3+}$ and $O^{2-}$ was not confirmed in the molten salt by absorption spectroscopy. The result of XRD for the solidified sample containing $Ti^{3+}$ and $O^{2-}$ implies that $O^{2-}$ reacts with $Ti^{3+}$ and $Cl^-$ to form TiOCl(s). The concentration quotient of the equilibrium between titanium ions ($Ti^{2+}$, $Ti^{3+}$) and metallic Ti, $K_c$, was revaluated at 740 °C as follows:

$$3Ti^{2+} \rightleftarrows 2Ti^{3+} + Ti,$$
$$K_c = 8.0 \times 10^{-2} \text{ mol L}^{-1} = 1.2 \times 10^{-1} \text{ mol kg}^{-1}.$$

In addition, the solubility product of TiOCl(s) in NaCl–KCl equimolar molten salt, $K_{sp}$, at 700 °C was determined using the results of absorption spectra,

$$K_{sp} = 1.2 \times 10^{-2} \text{ mol}^2 \text{ L}^{-2} = 5.1 \times 10^{-3} \text{ mol}^2 \text{ kg}^{-2}.$$

## 1. Introduction

Electroplating of titanium on base metals in molten salts is desired for some properties, such as improving corrosion resistance, so that many researchers investigated it [1–10]. However, the practical process of titanium electroplating has not been attained since the mechanism of the electrodeposition of titanium in molten salts is too complicated to control the morphology of the deposits. The complexity of the mechanism is caused by the oxidation states of titanium ions [9]. $Ti^{2+}$, $Ti^{3+}$ and $Ti^{4+}$ can exist together in molten salts. Thus, the understanding of the concentrations of each titanium ion in equilibrium with metallic titanium is critical to consider the mechanism. Several researchers investigated the concentration of titanium ions [11–14]. Mellgren and Opie pointed that the concentrations of titanium ions in molten salt is controlled by the following reaction [11]:

$$3Ti^{2+} \rightleftarrows 2Ti^{3+} + Ti. \tag{1}$$

They confirmed that the predominant titanium ion is $Ti^{2+}$ but there is a significant amount of $Ti^{3+}$ in $SrCl_2$–NaCl molten salt by chemical method, which contains the continuous two-step processes consisting of the hydrogen evolution and the titration. On the other hand, the concentration of $Ti^{4+}$ is negligible. Other researchers also investigated the concentration of titanium ions in molten salts and obtained similar conclusion [12–14].

The concentration quotient of reaction (1) evaluated using the results of the chemical analysis, $K_c^{\prime \text{analytical}}$, is expressed by the following equation:

$$K_c^{\prime \text{analytical}} = \frac{(x_{Ti^{3+}}^{\text{analytical}})^2}{(x_{Ti^{2+}}^{\text{analytical}})^3}, \tag{2}$$

where $x_{Ti^{2+}}^{\text{analytical}}$ and $x_{Ti^{3+}}^{\text{analytical}}$ are the cationic molar fraction of $Ti^{2+}$ and $Ti^{3+}$, respectively. Fig. 1 shows the relation between concentration quotient and the concentration of titanium ion in the literatures [11–14]. Considering the Henry's law, the concentration quotient should be constant in the region where the concentrations of titanium ions are low. However, the concentration quotient, $K_c^{\prime \text{analytical}}$, depends on the concentration of titanium ion as shown in Fig. 1. The concentration quotient increases with decreasing the
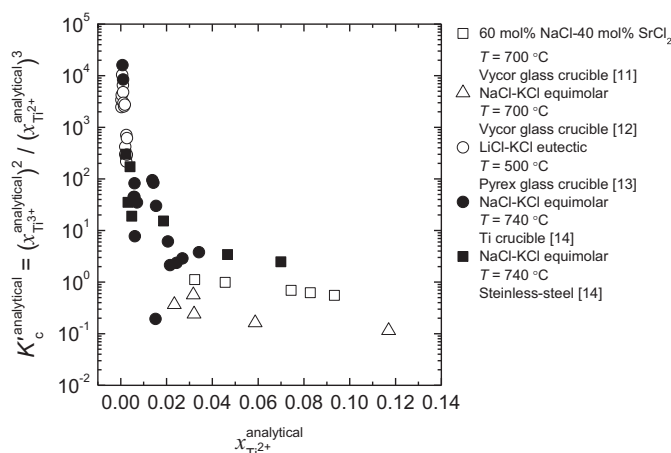
**Fig. 1.** Relation between the concentration quotient and the concentration of $Ti^{2+}$ in the literatures [11–14].

concentration of $Ti^{2+}$. Such a tendency indicates that there is an underestimation of the concentration of $Ti^{2+}$ or an overestimation of the concentration of $Ti^{3+}$. This could be caused by some systematic errors or by the effect of some impurities in molten salt. In previous paper, we reported that the systematic error in the chemical analysis was negligible [14]. Therefore, some impurities initially contained in molten salt could affect equilibrium (1). A considerable impurity is oxide ion, $O^{2-}$.

In this study, we thus determined the concentration of $O^{2-}$ in NaCl–KCl molten salt. Then, it was investigated that the effect of oxide ion on the equilibrium between titanium ions and metallic titanium in NaCl–KCl equimolar molten salt by absorption spectroscopy. Finally, the concentration quotient of titanium ions and metallic titanium was revaluated and discussed.

## 2. Concentration of oxide ion in NaCl–KCl equimolar molten salt

The concentration of oxygen in the mixture of NaCl and KCl was measured with nitrogen/oxygen combustion analyzer (EMGA-923, Horiba ltd., Kyoto). Samples were prepared by five procedures. Table 1 shows the procedures of the samples and the concentration of oxide ion in their samples. In this study, it is considered that all amount of oxygen species exists as oxide ion, $O^{2-}$, in molten salt. It was confirmed that the concentration of $O^{2-}$ remarkably decreased by drying at 200 °C in vacuo as shown in NK-b. The concentration of $O^{2-}$ in NK-d is higher than that in NK-c. This implies that the contamination of $O^{2-}$ comes from the oxide film on the surface of stainless-steel. Actually, the color of the sample NK-d was faint pink, while the color of the other samples was transparent or white. This suggests that NK-d contains something cation of the elements consisting of stainless-steel by the dissolution of the oxide film. Consequently, it is concluded that the concentration of oxide ion in NaCl–KCl molten salt is about 800 and 1500 ppm in the case using titanium container and using stainless-steel container, respectively.

## 3. Reaction between $Ti^{3+}$ and $O^{2-}$

### 3.1. Procedure

Fig. 2 shows the schematic illustration of the experimental apparatus for absorbance measurement. The detail of the optical system is described in the literature [15]. The electric furnace and the
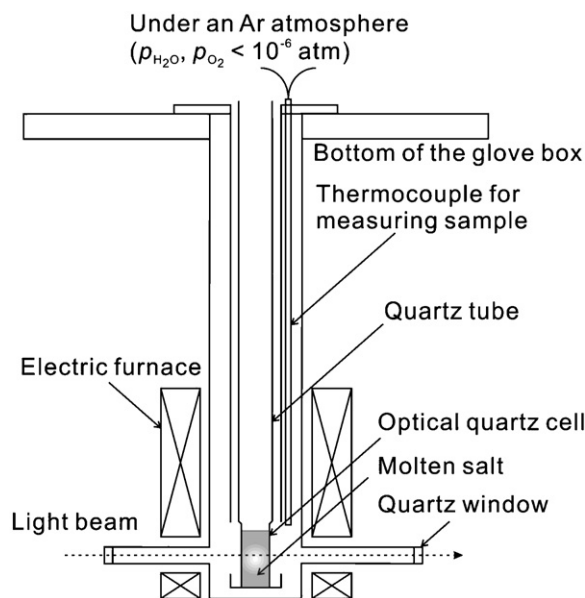


**Fig. 2.** Experimental apparatus for absorbance measurement of molten salt at high temperature.

setup for the spectroscopic experiments are attached on the bottom of the glove box, and the spectroscopic experiments were conducted in the Ar filled glove box, where the concentration of oxygen and water were maintained under 1 ppm. The weighted sample of NaCl–KCl equimolar mixture, NK-c, was inserted in the optical quartz cell. Then, the sample was heated to melt at 700 °C in the electric furnace. After the intensity of the transmitted light became stable, the spectroscopic measurement to the molten salt was carried out. Then, $TiCl_3$, which is purified by distillation from the mixture of $TiCl_3$ and $AlCl_3$ (76–78.5% as $TiCl_3$, Alfa Aesar, cat. #36729), was added into the molten salt and the intensity of the transmitted light was measured. This procedure was repeated several times for the measurement with various concentration of $TiCl_3$. From the difference between the intensity of the transmitted light passed through NaCl–KCl equimolar molten salt and that through $TiCl_3$–NaCl–KCl molten salt, the absorbance was calculated. Finally, a pellet of 2 mol% $Na_2O$–NaCl–KCl molten salt, which was prepared using NK-b and $Na_2O$ synthesized from metallic sodium and NaOH [16], was introduced to the molten salt as a source of $O^{2-}$, and the spectroscopic measurement on the molten salt was carried out to investigate the soluble ion of $Ti^{3+}$ and $O^{2-}$. After the spectroscopic experiments, the molten salt was quenched into room temperature and analyzed by X-ray diffractmeter (X'Pert PRO, PANalytical, Almelo).

### 3.2. Results

Fig. 3 shows the absorption spectra of the molten salts. The nominal concentration of $Ti^{3+}$ in mol $L^{-1}$ is represented as $C_{Ti^{3+}}^{nominal}$. The spectra have an absorption peak at 786 nm whose absorbance depends on $C_{Ti^{3+}}^{nominal}$. This peak attributes to the chloro complex of trivalent titanium ion [17]. Fig. 4 shows the absorption spectra of the molten salt before and after addition of $O^{2-}$. No additional peak attributing to the soluble species was confirmed, while the absorbance at 786 nm decreased. This indicates that the concentration of the chloro complex decreases. Additionally, there could be no soluble species except for the chloro complex in the molten salt. Fig. 5 shows the photographs of the $TiCl_3$–NaCl–KCl molten salts before and after addition of $O^{2-}$. $TiCl_3$–NaCl–KCl molten salt was a clear green liquid. When $O^{2-}$ was introduced into the molten

**Table 1**
The equimolar mixtures of NaCl and KCl.

| Sample # | Procedure | Concentration of $O^{2-}$ | |
|---|---|---|---|
| | | ppm | mol L$^{-1}$ |
| NK-a | Reagents of NaCl (GR, Nacalai tesque) and KCl (GR, Nacalai) were mixed. | 1900 | 0.183 |
| NK-b | The mixed reagents were dried at 200 °C in vacuo for more than 24 h. | 790 | 0.076 |
| NK-c | The NK-b in cylindrical quartz tube was dried at 400 °C in vacuo for 2 h, and then melted at 700 °C. After that, it was quenched into the air. | 820 | 0.079 |
| NK-d | The NK-b was melted at 700 °C in closed stainless-steel container filled with Air, and then quenched into the water. | 1480 | 0.142 |
| NK-e | The NK-b was melted at 700 °C in closed titanium container filled with Ar, and then quenched into the water. | 760 | 0.073 |
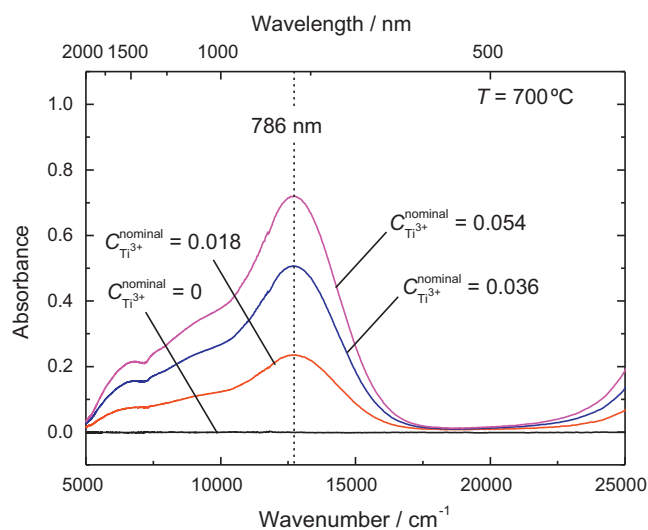


**Fig. 3.** Absorbance of TiCl$_3$–NaCl–KCl molten salt.
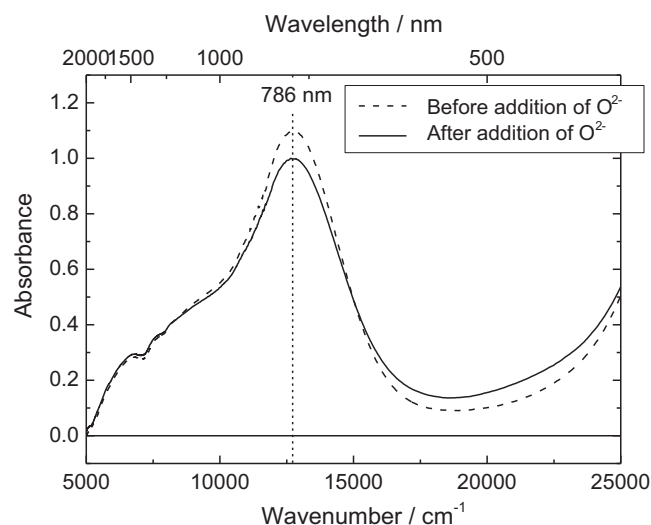


**Fig. 4.** Absorbance of TiCl$_3$–NaCl–KCl molten salt before and after addition of oxide ion.

salt, black particles formed as shown in Fig. 5(b). Therefore, it is considered that a part of the chloro complex transferred to the solid compound by the introduction of $O^{2-}$. Fig. 6 shows the result of XRD analysis of the solidified sample of molten salt containing the black precipitates. The result implies that the black particles was titanium oxychloride, TiOCl(s). Thus, it is concluded that Ti$^{3+}$ reacted with $O^{2-}$ and Cl$^-$ to form TiOCl(s) in molten salt.

## 4. Concentration quotient of titanium ions and metallic titanium

In this section, the effect of $O^{2-}$ on the concentration quotient of the equilibrium between titanium ions and metallic titanium

is investigated. Haarberg et al. reported that sludge formed when TiCl$_3$ and metallic titanium foil were added into LiCl–KCl eutectic molten salt [18]. They concluded that the sludge was metallic titanium particle since it was insoluble to hydrogen chloride solution. However, they did not consider the effect of oxide ion. Actually, the significant concentration of $O^{2-}$ was observed in molten salt as shown in Section 2. The reaction of Ti$^{3+}$ and $O^{2-}$ could also occur in the existence with metallic titanium in molten salt. Therefore, the sludge might be TiOCl(s), which was also insoluble in HCl aq. Consequently, the equilibrium between titanium ions and metallic titanium should be discussed in the existence with TiOCl(s). The concentration quotient is revaluated because the concentration of Ti$^{3+}$ might be overestimated in the reported experiments
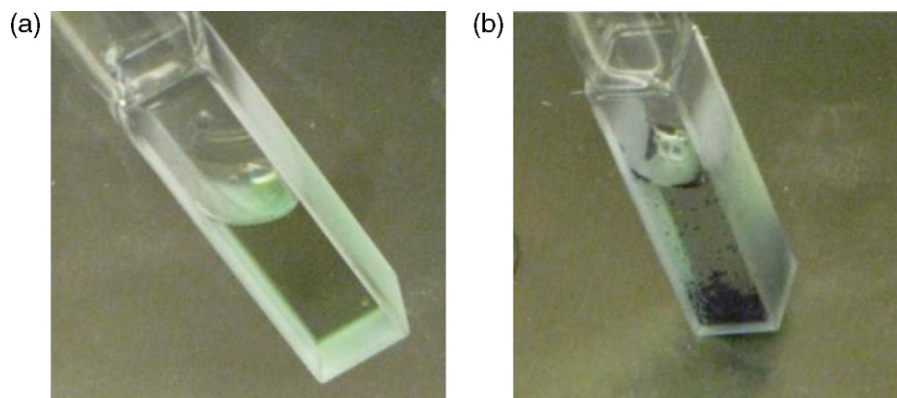


**Fig. 5.** Photographs of TiCl$_3$–NaCl–KCl molten salt (a) before and (b) after addition of oxide ion.
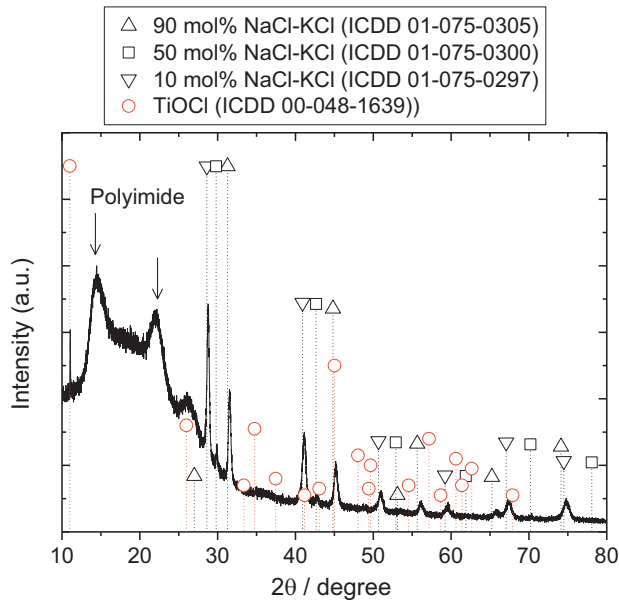
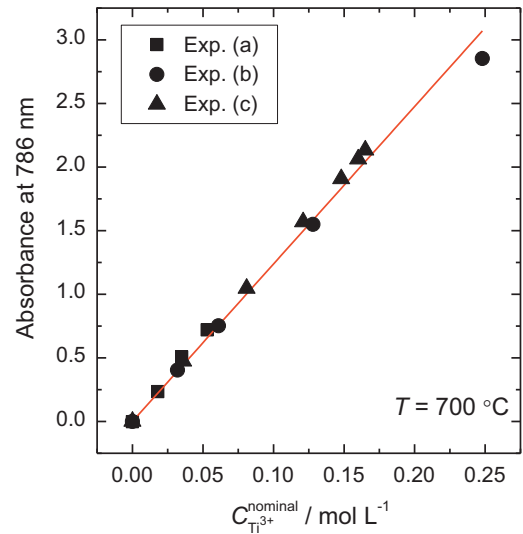**Fig. 6.** XRD pattern of the solidified molten salt containing the black precipitates.



**Fig. 7.** Relation between the absorbance at 786 nm and the nominal concentration of $Ti^{3+}$. Exp. (a), (b) and (c) corresponds to each experimental batch.

because $Ti^{3+}$ in molten salt and TiOCl(s) cannot be distinguished by the chemical analysis.

### 4.1. Expressions on the concentration quotient and the solubility product

The concentration quotient of reaction (1) in the existence of TiOCl(s), $K_c$, is described as follows:

$$K_c = \frac{(C_{Ti^{3+}}^{eq1})^2}{(C_{Ti^{2+}}^{eq1})^3}, \tag{3}$$

where $c_i^{eq1}$ is the equilibrium concentration of the species, $i$. From the result of absorption spectroscopy described in Section 3.2, TiOCl(s) dissolves in NaCl–KCl equimolar molten salt as follows:

$$TiOCl(s) \rightleftarrows Ti^{3+} + O^{2-} + Cl^-. \tag{4}$$

The equilibrium constant of reaction (4), $K_{eq}$, is defined by the following equation:

$$K_{eq} = \frac{a_{Ti^{3+}} a_{O^{2-}} a_{Cl^-}}{a_{TiOCl_{(s)}}}, \tag{5}$$

where $a_i$ is the activity of the species, $i$. The activities of chloride ion and TiOCl(s) are considered to be unity. The activity coefficients of $Ti^{3+}$ and $O^{2-}$ could be constant because the solubility of TiOCl(s) might be small. Thus, the solubility product of reaction (4), $K_{sp}$, is represented as follows:

$$K_{sp} = C_{Ti^{3+}}^{eq1} C_{O^{2-}}^{eq1}. \tag{6}$$

The relationships between the equilibrium concentration, $C_{Ti^{2+}}^{eq1}$ and $C_{Ti^{3+}}^{eq1}$, and the concentration of titanium ions evaluated by the chemical methods, $C_{Ti^{2+}}^{analytical}$ and $C_{Ti^{3+}}^{analytical}$, are as follows:

$$C_{Ti^{2+}}^{analytical} = C_{Ti^{2+}}^{eq1}, \tag{7}$$

$$C_{Ti^{3+}}^{analytical} = C_{Ti^{3+}}^{eq1} + C_{TiOCl}^{eq1}. \tag{8}$$

The mass balance of oxide ion is represented by the following equation:

$$C_{O^{2-}}^{initial} = C_{O^{2-}}^{eq1} + C_{TiOCl_{(s)}}^{eq1}, \tag{9}$$

where $C_{O^{2-}}^{initial}$ is the concentration of oxide ion initially contained in molten salt. Considering Eqs. (6), (8) and (9), the equilibrium concentration of $Ti^{3+}$ in the existence with TiOCl(s) should satisfy the following equation:

$$(C_{Ti^{3+}}^{eq1})^2 + (C_{O^{2-}}^{initial} - C_{Ti^{3+}}^{analytical})C_{Ti^{3+}}^{eq1} - K_{sp} = 0. \tag{10}$$

Therefore, $C_{Ti^{3+}}^{eq1}$ is calculated by Eq. (11) using $C_{Ti^{3+}}^{analytical}$, $C_{O^{2-}}^{initial}$ and $K_{sp}$,

$$C_{Ti^{3+}}^{eq1} = \frac{-(C_{O^{2-}}^{initial} - C_{Ti^{3+}}^{analytical}) + \sqrt{(C_{O^{2-}}^{initial} - C_{Ti^{3+}}^{analytical})^2 + 4K_{sp}}}{2}. \tag{11}$$

Thus, the calculation of evaluation of $C_{Ti^{3+}}^{eq1}$ needs the solubility product of TiOCl(s).

Here, we consider the equilibrium expressed by reaction (4) and determine $K_{sp}$. As we added TiOCl(s) into NaCl–KCl equimolar molten salt, the molten salt contains initial oxide ion and oxide ion by dissolution of TiOCl(s). The concentration of $O^{2-}$ is calculated as follows from the mass balance of oxide ion,

$$C_{O^{2-}}^{eq2} = C_{Ti^{3+}}^{eq2} + C_{O^{2-}}^{initial}, \tag{12}$$

where $C_i^{eq2}$ is the concentration of the species, $i$, in equilibrium with TiOCl(s). Therefore, the solubility product is calculated by the following equation:

$$K_{sp} = C_{Ti^{3+}}^{eq2}(C_{Ti^{3+}}^{eq2} + C_{O^{2-}}^{initial}). \tag{13}$$

### 4.2. Solubility product of TiOCl(s)

In this study, $C_{Ti^{3+}}^{eq2}$ was evaluated by in situ measurement using absorption spectroscopy. First, the analytical standard curve was evaluated for the quantitative analysis of the concentration of $Ti^{3+}$. In absorption spectra, consequently, the absorbance at 786 nm was used. Fig. 7 shows the relationship between the absorbance and the nominal concentration. The density of the $TiCl_3$–NaCl–KCl molten salt was approximated by that of NaCl–KCl equimolar molten salt.
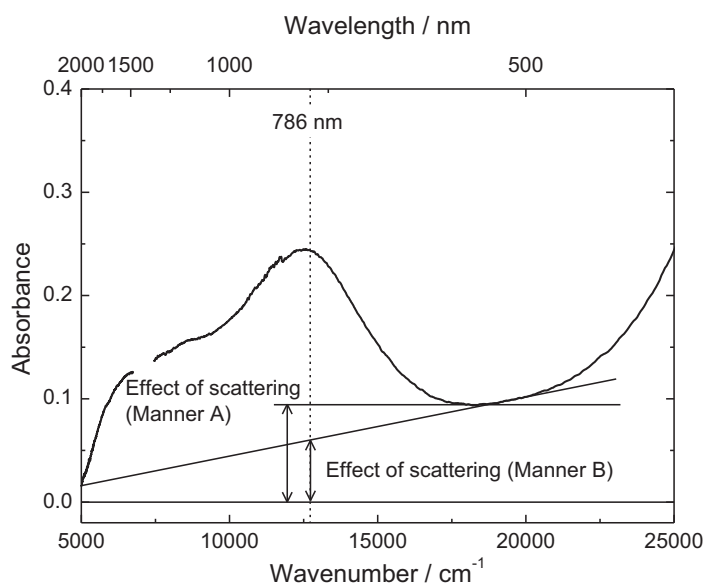
**Fig. 8.** The absorption spectrum obtained from the NaCl–KCl molten salt containing TiOCl(s).



**Fig. 9.** Revaluated concentration quotient considering the effect of $O^{2-}$. $n_i$ is mol of the species, $i$, in the unit volume of the molten salt.

As shown in the figure, a liner relation was reproducibly obtained in all experiments.

Next, the molten salt containing TiOCl(s) was investigated. TiOCl(s) used in this study was synthesized in our laboratory through the reaction of TiCl$_3$ and Ti$_2$O$_3$. We confirmed that the sample consists of a single phase of TiOCl(s) by XRD. The molten salt containing Ti$^{3+}$ and O$^{2-}$ in equilibrium with TiOCl(s) was obtained by the dissolution of TiOCl(s) into NaCl–KCl equimolar molten salt at 700 °C. The absorption spectrum was measured by the same procedure as described in Section 3.1, and $C_{Ti^{3+}}^{eq2}$ was evaluated using the analytical standard curve established in this study.

Fig. 8 shows the absorption spectrum of the NaCl–KCl equimolar molten salt containing TiOCl(s). The existence of the absorption peak at 786 nm indicates that TiOCl(s) dissolved in the molten salt to form Ti$^{3+}$. The concentration of Ti$^{3+}$ in equilibrium with TiOCl(s) was evaluated from the absorbance at 786 nm. Here, the absorbance at around 500 nm is larger than that in Fig. 3. It is considered that such an increase of the absorbance is caused by the scattering of the light beam by small particles suspended in the molten salt. Thus, the effect of scattering was evaluated by two manners as shown in Fig. 8.

The concentrations of Ti$^{3+}$ in equilibrium with TiOCl(s) corrected by the manners A and B were 0.012 mol L$^{-1}$ and 0.015 mol L$^{-1}$, respectively. The solubility product of TiOCl(s), $K_{sp}$, was calculated to be $1.2 \times 10^{-3}$ mol$^2$ L$^{-2}$ using Eq. (13) from the median of the concentrations of Ti$^{3+}$ and the concentration of O$^{2-}$ in NK-c: $C_{Ti^{3+}}^{eq2} = 0.0135$ and $C_{O^{2-}}^{initial} = 0.0925$.

### 4.3. Revaluation of concentration quotient

Fig. 9 shows the relation between the concentration quotient revaluated using $K_{sp}$ at 740 °C. Here, it is assumed that the solubility product of TiOCl(s) is not different between at 700 °C and at 740 °C. The initial concentration of O$^{2-}$ in the experiment using stainless-steel container and titanium container corresponds to the values of NK-d and NK-e in Table 1, respectively. The revaluated concentration quotient, $K_c$, seems to be constant in the range from 0.1 to 2.0 mol L$^{-1}$ using stainless-steel container, while it shows relatively large dispersion using Ti container. Thus, the stainless-steel container is suitable for the equilibrium experiments on titanium ions and metallic titanium. The concentration quotient
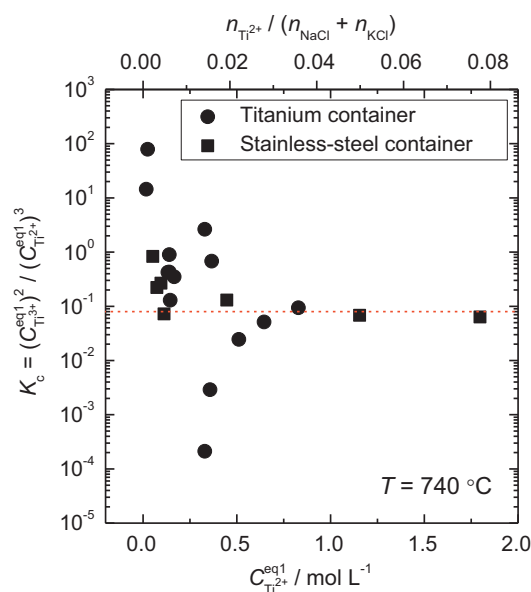
is still scattered upwardly where $C_{Ti^{2+}}^{eq1} < 0.1$ mol L$^{-1}$ even when considering the effect of oxide. The reason is not clarified, but we guess that something systematic errors, such as the oxidation of titanium ions in sample during sample treatment, are not negligible because the total amount of titanium ions in sample might be very small in the range. Therefore, it is concluded that titanium ions co-existence with metallic titanium are also in equilibrium with TiOCl(s). Fig. 9 shows that the value of the concentration quotient is $8.0 \times 10^{-2}$ mol L$^{-1}$ at 740 °C. Here, it is convenient that the concentration of titanium ions is represented in molar fraction rather than in molarity. Since the total amount of titanium ions in the molten salt are much smaller than that of Na$^+$ and K$^+$, the total mol of cation in the molten salt could be approximated by that of Na$^+$ and K$^+$. We thus assumed that the density of the molten salt used in this study was same as that of the NaCl–KCl equimolar molten salt, which was 1.56 g cm$^{-1}$ at 740 °C [19]. The determined concentration quotient of reaction (1) is re-calculated to be 1.9 in cationic molar fraction at 740 °C.

### 5. Conclusions

In this study, the effect of O$^{2-}$ on the equilibrium between titanium ions and metallic titanium was investigated by absorption spectroscopy. As the results, the following conclusions were obtained.

1. The solubility product of TiOCl(s) in NaCl–KCl equimolar molten salt was evaluated to be $1.2 \times 10^{-3}$ mol$^2$ L$^{-2}$ at 700 °C.
2. The concentration quotient of the equilibrium between titanium ions and titanium was re-evaluated using the reported data. The revaluated concentration quotient shows constant value in the range from 0.01 to 2.0 mol L$^{-1}$. When the unit of the concentrations of titanium ions is mol L$^{-1}$, the value of the concentration quotient is $8.0 \times 10^{-2}$ mol L$^{-1}$ at 740 °C.

## References

[1] M.E. Sibert, M.A. Steinberg, J. Electrochem. Soc. 102 (1955) 641.
[2] A. Brenner, S. Senderoff, J. Electrochem. Soc. 99 (1952), 223C.
[3] B.J. Fortin, J.G. Wurm, L. Gravel, R.J.A. Potovin, J. Electrochem. Soc. 106 (1959) 428.
[4] A.W. Schlechten, M.E. Straumanis, C.B. Gill, J. Electrochem. Soc. 102 (1955) 81.
[5] S. Tokumoto, E. Tanaka, K. Ogisu, J. Met. 27 (1975) 18.
[6] A. Robin, J. De Lepinay, M.J. Barbier, J. Electroanal. Chem. 230 (1987) 125.
[7] T. Oki, Molten Salts 37 (1994) 167.
[8] H. Takamura, I. Ohno, H. Numata, J. Jpn. Inst. Met. 60 (1996) 388.
[9] A. Robin, R.B. Ribeiro, J. Appl. Electrochem. 30 (2000) 239.
[10] T. Uda, T.H. Okabe, Y. Waseda, Y. Awakura, Sci. Technol. Adv. Mater. 7 (2006) 490.
[11] S. Mellgren, W. Opie, J. Met. 9 (1957) 266.
[12] W.C. Kreye, H.H. Kellog, J. Electrochem. Soc. 104 (1957) 504.
[13] H. Takamura, I. Ohono, H. Numata, J. Jpn. Inst. Met. 60 (1996) 382.
[14] H. Sekimoto, Y. Nose, T. Uda, H. Sugimura, Mater. Trans., JIM 51 (2010) 2121.
[15] T. Fujii, H. Moriyama, H. Yamana, J. Alloys Compd. 251 (2003) L6.
[16] The Chemical Society of Japan, The Fifth Series of Experimental Chemistry, Inorganic Compounds 23, Maruzen Co., Ltd., Tokyo, 2005 (in Japanese).
[17] D.M. Gruen, R.L. McBETH, Pure Appl. Chem. 6 (1963) 23.
[18] G.M. Haarberg, W. Rolland, Å. Sterten, J. Thonstad, J. Appl. Electrochem. 23 (1993) 217.
[19] The Committee of Fused Salt Chemistry, The Electrochemical Society of Japan (Eds.), Physico-Chemical Constants of Fused Salts, Kagakudojin, Kyoto, 1963, p. 283 (in Japanese).