Thermodynamics of Titanium Oxide in CaO–SiO$_2$–Al$_2$O$_3$–MgO$_{satd}$–CaF$_2$ Slag Equilibrated with Fe–11mass%Cr Melt

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Thermodynamic equilibrium between the CaO–SiO$_2$–Al$_2$O$_3$–MgO$_{satd}$–CaF$_2$–TiO$_x$ slags and the Fe–11mass%Cr melt was investigated at 1873 K in order to understand the thermodynamic behavior of titanium oxide in the refining slags. The equilibrium between silicon and titanium in steel melts and their oxides in the slags are theoretically expected and experimentally proved well. The activity coefficient of TiO$_2$ increases by increasing the basicity in logarithmic scale. By combining this with the previous results, in multi component calcium(–magnesium) silicate slags containing Al$_2$O$_3$ and TiO$_2$, TiO$_2$ could be considered as a basic oxide in silicate base melts, while it could be the relatively acidic oxide in the aluminate (very low silical base melts. The activity coefficient of TiO$_2$ gradually decreases by substituting silica for alumina, indicating that the attraction between TiO$_2$ and SiO$_2$ is greater than that between TiO$_2$ and Al$_2$O$_3$ in the present slag system. This could be explained from the electronegativity difference between each cation involved. The activity of TiO$_2$ in the 10mass%MgO slag system shows a negative deviation from an ideality, while that in the CaO–SiO$_2$–Al$_2$O$_3$–MgO$_{satd}$–CaF$_2$ system is relatively close to the ideal behavior up to about 10mol% TiO$_2$. This is mainly due to the relatively basic characteristic of TiO$_2$.

KEY WORDS: titanium oxide; activity; activity coefficient; electronegativity; negative deviation; ideal behavior.

1. Introduction

Titanium stabilized (stainless) steels have been the subject of previous studies related to clogging of the submerged entry nozzle (SEN) during continuous casting process.$^{1–5}$ In view of high yield of titanium during ladle treatment, the thermodynamic behavior of titanium oxide in the slag is also very important. Even though there are numerous studies in redox equilibria of titanium in glasses and geochemical silicate melts,$^{6–9}$ the thermodynamic behavior of titanium oxide in metallurgical slag system has not so clearly been understood yet.

Ito and Sano primarily calculated the activity coefficients of TiO$_{1.5}$ and TiO$_2$ (TiO$_{1.5}$) in the CaO–SiO$_2$–Al$_2$O$_3$–MgO slag (Blast Furnace (BF) type) system equilibrated with TiC and C under CO atmosphere from 1673 to 1823 K. However, they did not consider the formation reaction of TiC under strongly reducing conditions and thus the activity of TiO$_2$ would be underestimated, which resulted in the significantly negative deviation from an ideal behavior. Actually, the activity of TiO$_2$ in the slag was about 4 to 5 order lower than that measured by other researchers. Tranell et al.$^{12,13}$ estimated the activity coefficient ratio of TiO$_{1.5}$ and TiO$_2$ from the ratio of Ti$^{3+}$/ Ti$^{4+}$ in the CaO–SiO$_2$–MgO–Al$_2$O$_3$–TiO$_x$ slags at temperatures between 1783 and 1903 K under CO–CO$_2$–Ar atmosphere. Increasing the TiO$_2$ concentration from 7 to 52mass% resulted in a maximum in the $\gamma_{TiO_2}/\gamma_{TiO_{1.5}}$ ratio at 14mass% TiO$_2$ in the slag at given basicity and oxygen partial pressure. They explained this non-linear behavior might be originated form the formation of complex anions such as (TiO$_2$)$_2$$^{2–}$ rather than (TiO$_2$)$_4$$^{2–}$ simple tetrahedra at high TiO$_2$ concentrations. They also tried to analyze the effect of titanium on the structure of silicate system using Raman spectra.$^{14}$ Morizane et al.$^{15}$ measured the activity of TiO$_2$, and TiO$_{1.5}$ in the CaO–SiO$_2$–Al$_2$O$_3$–10mass%MgO BF type slag equilibrated with carbon saturated iron and a CO gas at 1773 K. Over the concentration range studied, the effect of TiO$_2$ (<7mass%) on its activity coefficient was small. An increase in the basicity at a given alumina concentration or a decrease in alumina at a given slag basicity was found to increase the $\gamma_{TiO_2}/\gamma_{TiO_{1.5}}$ ratio. However, in their experiments, the effect of alumina on the activity coefficient of TiO$_2$ would not be discernable even though the concentration of
alumina widely varied from 7 to 22 mass%. Jung and Fruehan estimated the activity and activity coefficient of TiO$_{1.5}$ and TiO$_2$ in the CaO–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ ladle type slags equilibrated with the Fe–C$_{satd}$–Ti(–Cr–Si) or Fe–Al–Ti melts at 1 873 K. The activity of TiO$_{1.5}$ exhibited a negative deviation from Raoult’s law, while a positive deviation was obtained for the activity of TiO$_2$, which is in contradiction to those obtained by Morizane et al. Jung and Fruehan also found that the amount (or stability) of TiO$_2$ in the slags was sufficiently high when the oxygen partial pressure was determined by [Al]–(Al$_2$O$_3$) equilibrium rather than by C–CO equilibrium. Even though Ariyo and Holappa also measured the activity of Ti$_2$O$_3$ (10 to 39 mass%) in the CaO–SiO$_2$–Ti$_2$O$_3$ slag system at 1 873 K, there was no clear tendency for the effect of basicity on the thermodynamic behavior of TiO$_{1.67}$. In the later work, they observed that the ratio of $\gamma$$_{TiO_2}$ to $\gamma$$_{TiO_3}$ in the CaO–SiO$_2$–TiO$_3$ slag (CaO/SiO$_2$ = 1.4) shows a maximum at about 30 mass% TiO$_2$, as the concentration of TiO$_3$ increases from 10 to 52 mass% at 1 873 K. This is similar to the result measured by Tranell et al. However, the almost of TiO$_3$ could be estimated as TiO$_2$ at oxygen partial pressure determined by CO–CO$_2$ equilibrium. From these previous studies, the effect of slag composition on the thermodynamic behavior of titanium oxide in the CaO–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ slags has not been clarified yet.

Consequently, in the present work, the thermodynamic equilibrium between the CaO–SiO$_2$–Al$_2$O$_3$–MgO$_{satd}$–5mass%CaF$_2$–(TiO$_3$) slag and the Fe–11mass%Cr melt was investigated at 1 873 K in order to understand the thermodynamic behavior of titanium oxide in the refining slags.

### 2. Experimental

Pure iron, chromium, silicon, and manganese (>99.9 mass% reagent grade Fe, Cr, Si, and Mn) were premelted in a vacuum induction furnace to make a nominal composition of Fe–11mass%Cr–0.5mass%Si–0.3mass%Mn steel. Alloys of about 730 g and the CaO–SiO$_2$–MgO–Al$_2$O$_3$–5mass%CaF$_2$–5mass%Fe–11mass%Cr slag (B=(mass% CaO+mass% MgO)/(mass% SiO$_2$)=1.6–5.8) of about 20–30 g were equilibrated in pure MgO (>99.9 mass%, MgO–S(3N), TEP Corp., Tokyo, Japan) crucibles at 1 873 K, heated in a high frequency induction furnace. The initial contents of dissolved aluminum and titanium were determined by [Al]–(Al$_2$O$_3$) and [Ti]–(TiO$_2$) equilibria.22) Consequently, in the present work, the thermodynamic equilibrium between the CaO–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ slags and the Fe–11mass%Cr melt was investigated at 1 873 K in order to understand the thermodynamic behavior of titanium oxide in the refining slags.

### 3. Results and Discussion

#### 3.1. Equilibrium between Slag and Metal Phases

Figure 2 exhibits the equilibrium between titanium and silicon in the steel and their oxides in the slag at 1 873 K based on the following reaction.
where \( K_{(1)} \) is the equilibrium constant of Eq. (1), and \( \gamma_i, X_i \) and \( a_i \) are, respectively, the activity coefficient, the mole fraction, and the activity of component \( i \). From Eq. (3), the term \( \log a_{Ni} - \log X_{TiO_2} \) is in direct proportion to the \( \log a_{Si} - \log X_{SiO_2} \) with a slope of unity assuming that the activity coefficient ratio of TiO\(_2\) to SiO\(_2\) would not so seriously be changed at a fixed temperature under equilibrium condition. Figure 2 shows a relationship between the \( \log a_{Ni} - \log X_{TiO_2} \) and the \( \log a_{Si} - \log X_{SiO_2} \) at 1 873 K, where a good linear correlation \( (r^2=0.87) \) with a slope of 1.1, which is close to the expected value of unity in Eq. (3). In the present study, the activity of metallic element such as silicon and titanium was calculated based on the following classical Wagner formalism using the first- and second-order interaction parameters, which are listed in Table 3.23–35)

\[
\log f_M = \sum_{i=Cr, Si, Mn, Al, Ti, O} \left( c^i_M \times \text{[mass%]} + r^i_M \times \text{[mass%]}^2 \right)
\]

where \( f_M \), \( c^i_M \), and \( r^i_M \) is, respectively, the Henrian activity coefficient of element M, and the first- and second-order interaction parameters between each element.

The equilibrium reaction between aluminum and titanium in molten steel and their oxides in the slag can also be investigated based on the following reaction.

\[
4\text{[Al]} + 3\text{(TiO}_2\text{)} = 2\text{(Al}_2\text{O}_3\text{)} + 3\text{[Ti]} ....(5)
\]

\[
K_{(5)} = \frac{\gamma_{Al}^2 \times X_{Al}_2O_3 \times a_{Ti}^3}{\gamma_{Ti}^3 \times X_{TiO}_2} ....(6)
\]

\[
3 \log a_{Ni} - 3 \log X_{TiO_2} = 4 \log a_{Al} - 2 \log X_{Al}_2O_3 + \log \frac{\gamma_{Al}^2}{\gamma_{Al}_2O_3} + \log K_{(5)} ....(7)
\]

Figure 3 exhibits a relationship between “3 \( \log a_{Ni} - 3 \log X_{TiO_2} \)” and “4 \( \log a_{Al} - 2 \log X_{Al}_2O_3 \)” at 1 873 K, where a good linear relationship \( (r^2=0.90) \) between them is ob-

| Table 1. Equilibrium composition of the slags in the present study (mass%). |
|---|
| Run | CaO | Al\(_2\)O\(_3\) | SiO\(_2\) | TiO\(_2\) | Ca\(_2\)F | MgO |
| 10M-0 | 42.6 | 6.1 | 19.5 | 14.7 | 6.7 | 10.4 |
| 10M-1 | 42.8 | 12.8 | 16.2 | 12.5 | 5.5 | 10.3 |
| 10M-2 | 44.2 | 15.7 | 14.8 | 11.4 | 4.2 | 9.7 |
| 10M-7 | 42.0 | 16.0 | 11.5 | 14.4 | 6.3 | 9.8 |
| 10M-8 | 43.0 | 18.7 | 9.0 | 13.1 | 6.9 | 9.3 |
| 18M-3 | 33.9 | 5.2 | 25.8 | 12.8 | 6.1 | 16.2 |
| 18M-4 | 31.5 | 7.6 | 26.1 | 12.1 | 4.1 | 18.5 |
| 18M-5 | 31.7 | 9.5 | 26.4 | 10.9 | 3.2 | 18.4 |
| 18M-6 | 31.3 | 12.1 | 25.5 | 9.8 | 3.8 | 17.4 |
| 18M-9 | 32.3 | 14.2 | 20.0 | 12.5 | 5.4 | 15.7 |
| 18M-10 | 31.4 | 16.1 | 19.0 | 12.2 | 5.1 | 16.2 |
| 18M-5A | 30.9 | 9.7 | 31.8 | 4.5 | 3.6 | 19.5 |

| Table 2. Equilibrium composition of the steel melts in the present study (mass%). |
|---|
| Run | Total O | Dissolved O | Total Al | Dissolved Al | Ti |
| 10M-0 | 0.0023 | 0.00200 | 0.0035 | 0.0007 | 0.036 |
| 10M-1 | 0.0029 | 0.00151 | 0.0035 | 0.0015 | 0.023 |
| 10M-2 | 0.0018 | 0.00134 | 0.0045 | 0.0021 | 0.035 |
| 10M-7 | 0.0032 | 0.00068 | 0.0074 | 0.0068 | 0.071 |
| 10M-8 | 0.0023 | 0.00057 | 0.0113 | 0.0110 | 0.100 |
| 18M-3 | 0.0023 | 0.00169 | 0.0020 | 0.0003 | 0.020 |
| 18M-4 | 0.0024 | 0.00216 | 0.0020 | 0.0003 | 0.013 |
| 18M-5 | 0.0024 | 0.00188 | 0.0021 | 0.0004 | 0.015 |
| 18M-6 | 0.0030 | 0.00183 | 0.0020 | 0.0004 | 0.010 |
| 18M-9 | 0.0024 | 0.00157 | 0.0045 | 0.0028 | 0.029 |
| 18M-10 | 0.0025 | 0.00167 | 0.0043 | 0.0022 | 0.024 |
| 18M-5A | 0.0034 | 0.00251 | 0.0017 | 0.0004 | 0.005 |

| Table 3. Interaction parameters used in the present study. |
|---|
| & (r) | Cr | Si | Mn | Al | Ti | O |
| Al | 0.030(27) | 0.056 | 0.035(30) | 0.043 | 0.016(30) | -1.98(30) |
| (39.82) |
| Ti | 0.029(28) | -0.025(31) | -0.043 | 0.024(31) | 0.049(31) | -1.62(31) |
| (-0.36) |
| Si | -0.021(29) | 0.10 | -0.007* | 0.058 | -0.013* | -0.12 |
| O | -0.032(28) | -0.066 | -0.037(31) | -1.17(31) | -0.54(31) | -0.17 |
| (-0.010) | (0.039) |

[Cr]=11.1(±0.1)mass%, [Si]=0.51(±0.09)mass%, [Mn]=0.29(±0.01)mass%
served. However, the slope of the line (0.5) is relatively lower than the expected value of unity, indicating that the activity coefficient term would be affected in the composition range investigated in the present study. The more detailed discussion for the effect of slag composition on the stability of titanium oxide will be given later in Sec. 3.2.

3.2. Effect of Slag Composition on Activity Coefficient of Titanium Oxide

The dependence of activity coefficient of TiO$_2$ ($\log \gamma_{\text{TiO}_2}$) on the basicity of slags $B$, which is defined as the ratio of (mass% CaO) to (mass% MgO) to (mass% SiO$_2$), is shown in Fig. 4. The measured results by Ito and Sano,10) Morizane et al.,15) Jung and Fruehan,16) and Ariyo and Holappa17,18) are compared to the present value. In the present study, the activity coefficient of TiO$_2$ could be calculated from the following equilibrium reaction.26,36)

$$[\text{Ti}] + 2[\text{O}] = (\text{TiO}_2) \quad \text{ ............(8)}$$

$$\Delta G^\circ = -659880 + 2297 \ T \text{ (J/mol)} \quad \text{ ............(9)}$$

$$\log \gamma_{\text{TiO}_2} = \log a_{\text{Ti}} - 2 \log a_{\text{O}} + K_B - \log X_{\text{TiO}_2} \quad \text{ ............(10)}$$

The activity of titanium and oxygen in molten steel was calculated from Eq. (4) and Table 3.22) Especially, the concentration of dissolved oxygen was taken by the average value of oxygen determined from $[\text{Al}]-([\text{Al}_2\text{O}_3]$ and $[\text{Si}]-([\text{SiO}_2]$ equilibria.22) The present value of $\log \gamma_{\text{TiO}_2}$ increases by increasing the $B$, which is on the extended line estimated by Ito and Sano. The activity coefficient of TiO$_2$, $\log \gamma_{\text{TiO}_2}$ measured by Ariyo and Holappa is also on this line. On the other hand, the log $\gamma_{\text{TiO}_2}$ calculated by Jung and Fruehan exhibits a maximum at about $B = 0.7$ with some scatters. Consequently, a dashed trend could be derived through the wide basicity range, excluding the activity coefficient of TiO$_2$ measured by Morizane et al. This means that, in multi component calcium–magnesium) silicate slags containing 5 to 30 mass% Al$_2$O$_3$ and about 15 mass% TiO$_2$, the TiO$_2$ could be considered as a basic oxide in silicate base melts, while it could be the relatively acidic oxide in the aluminate (very low silica) base melts. Duan et al.37,38) realized that the TiO$_2$ in the CaO–SiO$_2$–Al$_2$O$_3$ (silica>50 mass%) glasses could be a network modifier in the form of [TiO$_2$]-octahedron at high temperatures, whereas it becomes a network former in the form of [TiO$_3$]-tetrahedron at low temperatures close to glass transition temperature ($T_g$). This tendency is in good accordance with a decrease in viscosity by addition of small amount of TiO$_2$ to the CaO–SiO$_2$–Al$_2$O$_3$–MgO ($B = 0.8$ to $1.4$, recalculated from their compositions in order to compare Fig. 4) slag system at 1673 to 1873 K, which was recently measured by Shankar et al.39) Saito et al.40) also reported that a viscosity of the CaO–SiO$_2$–Al$_2$O$_3$ ($B = 1.0$) slags decreases by addition of TiO$_2$.

The opposite tendency of the activity coefficient of TiO$_2$ reported by Morizane et al.15) to the others could be occurred during the calculation of the $\gamma_{\text{TiO}_2}$, as shown in Morizane et al.’s paper. They calculated the $\gamma_{\text{TiO}_2}$, using the equilibrium constant of the TiO$_2$–C equilibrium reaction (TiO$_2$(s) + C(s) = Ti(s) + CO(g); Eq. (20) in Ref. 15)) and the Henrian activity coefficient of titanium ($f_T$) in carbon saturated iron. They used the value of $f_T = 0.023$ at 1773 K (Eq. (22) in Ref. 15)), even though the concentration of titanium and silicon in the metal phase would be varied by slag compositions in equilibrium conditions. However, unfortunately, the composition of metal and slag for the full experimental heats are not available in their study.

Figure 5 shows a substitution effect of silica for alumina on the activity coefficient of TiO$_2$ in the slags at 1873 K. The log $\gamma_{\text{TiO}_2}$ gradually decrease by increasing the ratio of (mass% SiO$_2$) to (mass% Al$_2$O$_3$). This indicates that the attraction between TiO$_2$ and SiO$_2$ is greater than that between TiO$_2$ and Al$_2$O$_3$ in the present slag system, which could be expected from the electronegativity difference between each cation involved ($\varepsilon_\text{Si}=1.8$, $\varepsilon_\text{Al}=1.5$)41) as reported by Park and Min.42) That is, the greater the difference in the electronegativity between each cation, the more ionic characteristics of the chemical bond between them in the slags.

Figure 6 exhibits the effect of TiO$_2$ concentration and the S(S+A) ratio on the activity coefficient of TiO$_2$ in the slags at 1873 K. At relatively low S(S+A) ratio less than about 0.6, the log $\gamma_{\text{TiO}_2}$ linearly increases with increasing concentration of TiO$_2$, while it shows a minimum at about $X_{\text{TiO}_2} = 0.08$ at relatively high S(S+A) ratio greater than...
about 0.6. Tranell et al.\textsuperscript{12,14} suggested that the complex behavior of titanium oxide, which shows a minimum Ti\textsuperscript{3+}/Ti\textsuperscript{4+} or maximum $g_{\text{TiO}_1.5}/g_{\text{TiO}_2}$ ratio as a function of TiO\textsubscript{x} concentration could be attributed to the effect of total amount of titanium on the structure of silicate melts containing titanium oxide. They observed from the Raman spectra that, with increasing TiO\textsubscript{x} concentration, the proportion of polymerized titanate units (chains) increases, while the proportion of depolymerized units (monomers) decreases. However, because there are insufficient experimental data in the region of relatively low SiO\textsubscript{2} and TiO\textsubscript{2} concentrations, the conclusive remarks for the effect of TiO\textsubscript{2} concentration on the stability of titanate anion complexes are still remained for further discussion.

The activity of TiO\textsubscript{2} is shown in Fig. 7 as a function of TiO\textsubscript{2} concentration in the slags at 1 873 K. The measured results by Morizane et al.,\textsuperscript{15} Jung and Fruehan,\textsuperscript{16} and Ariyo and Holappa\textsuperscript{17,18} are compared to the present value. The activity of TiO\textsubscript{2} in the CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO\textsubscript{satd}–CaF\textsubscript{2} slag system measured by Morizane et al. at 1 773 K is extrapolated to 1 873 K based on the regular solution assumption for comparison. The activity of TiO\textsubscript{2} in this slag system shows a negative deviation from an ideality, while that in the CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO\textsubscript{satd}+Fe\textsubscript{2}O\textsubscript{3} system measured by Jung and Fruehan, and by the present authors is close to the ideal behavior up to about $X_{\text{TiO}_2}$=0.1. This is mainly due to the basic characteristic of TiO\textsubscript{2} as discussed previously in Fig. 4. Also, the activity of TiO\textsubscript{2} measured by Ariyo and Holappa qualitatively follows the Raoult’s law at high TiO\textsubscript{2} concentration region.

In summary, the present slag–metal equilibrium experiments could provide the useful information regarding the thermodynamic behavior of TiO\textsubscript{2} in the slags and especially the effect of slag composition on it. The TiO\textsubscript{2} behaves as a network modifying basic oxide in the silicate base melts such as BF slags and mold fluxes, whereas it behaves as a network forming acidic oxide in the aluminosilicate base melts used in secondary refining processes. However, the effect of TiO\textsubscript{2} concentration on the stability of TiO\textsubscript{2} in the slag is still in a room for further discussion including structural studies.

4. Conclusions

The thermodynamic equilibrium between the CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO\textsubscript{satd}–CaF\textsubscript{2} slags and the Fe–11mass%Cr melt was investigated at 1 873 K in order to understand the thermodynamic behavior of titanium oxide in the refining slags. The conclusions in the present study are summarized as follows.

(1) The equilibrium between silicon and titanium in steel melts and their oxides in the slags are theoretically expected and experimentally proved well.

(2) The value of log $g_{\text{TiO}_2}$ increases by increasing the log $g_{\text{SiO}_2}$, which is on the extended line estimated by Ito and Sano. By combining this with the previous results, in multicomponent calcium (–magnesium) silicate slags containing 5 to 30 mass% Al\textsubscript{2}O\textsubscript{3} and to about 15 mass% TiO\textsubscript{2}, the TiO\textsubscript{2} could be considered as a basic oxide in silicate base melts, while it could be the relatively acidic oxide in the aluminosilicate (very low silica) base melts.

(3) The log $g_{\text{TiO}_2}$ gradually decrease by increasing the ratio of (mass% SiO\textsubscript{2})/(mass% SiO\textsubscript{2}/mass% Al\textsubscript{2}O\textsubscript{3}), indicating that the attraction between TiO\textsubscript{2} and SiO\textsubscript{2} is greater than that between TiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} in the present slag system. This could be explained from the electronegativity difference between each cation involved.

(4) The activity of TiO\textsubscript{2} in the slag system containing 10 mass% MgO shows a negative deviation from an ideal-
ity, while that in the CaO–SiO$_2$–Al$_2$O$_3$–MgO$_{satd}$–(CaF$_2$) system is relatively close to the ideal behavior up to about $X_{TiO_2}=0.1$. This is mainly due to the relatively basic characteristic of TiO$_2$.

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