Thermodynamics of Titanium Oxide in CaO–SiO₂–Al₂O₃–MgO_{satd}–CaF₂ Slag Equilibrated with Fe–11mass%Cr Melt

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Thermodynamic equilibrium between the CaO–SiO₂–Al₂O₃–MgO_{satd}–CaF₂(–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 TiO₂ increases by increasing the basicity in logarithmic scale. By combining this with the previous results, in multi component calcium(–magnesium) silicate slags containing Al₂O₃ and TiO₂, TiO₂ 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. The activity coefficient of TiO₂ gradually decreases by substituting silica for alumina, indicating that the attraction between TiO₂ and SiO₂ is greater than that between TiO₂ and Al₂O₃ in the present slag system. This could be explained from the electronegativity difference between each cation involved. The activity of TiO₂ in the 10%MgO slag system shows a negative deviation from an ideality, while that in the CaO–SiO₂–Al₂O₃–MgO_{satd}(–CaF₂) system is relatively close to the ideal behavior up to about 10 mol% TiO₂. This is mainly due to the relatively basic characteristic of TiO₂.

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} ($\gamma_{\text{TiO}_{1.5}}$) and TiO₂ (γ_{TiO_2}) in the CaO–SiO₂–Al₂O₃–MgO slag (Blast Furnace (BF) type) system equilibrated with TiC and C under CO atmosphere from 1673 to 1823 K on the basis of the equilibrium concentration of Ti³⁺ and Ti⁴⁺ ions.¹⁰⁾ The TiO₂ was found to behave amphoterically with the critical CaO/SiO₂ ratio equal to unity. The TiO_{1.5} behaves as a basic oxide except in low (<15 mass%) silica system, where it turns out to behave as an acidic oxide. Benesch *et al.*¹¹⁾ tried to evaluate the activity of TiO₂ (<14 mass%) in the CaO–SiO₂–Al₂O₃–MgO BF type slags equilibrated with carbon saturated iron at temperatures from 1723 to 1823 K. However, they did not consider the formation reaction of TiC under strongly reducing

conditions and thus the activity of TiO₂ would be underestimated, which resulted in the significantly negative deviation from an ideal behavior. Actually, the activity of TiO₂ 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 TiO₂ from the ratio of Ti³⁺/Ti⁴⁺ in the CaO–SiO₂–MgO–Al₂O₃–TiO_x slags at temperatures between 1783 and 1903 K under CO–CO₂–Ar atmosphere. Increasing the TiO_x concentration from 7 to 52 mass% resulted in a maximum in the $\gamma_{\text{TiO}_{1.5}}/\gamma_{\text{TiO}_2}$ ratio at 14 mass% TiO_x in the slag at given basicity and oxygen partial pressure. They explained this non-linear behavior might be originated from the formation of complex anions such as (Ti₂O₆)^{4–} rather than (TiO₄)^{4–} simple tetrahedra at high TiO_x 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 TiO₂ and TiO_{1.5} in the CaO–SiO₂–Al₂O₃–10mass%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_x (<7 mass%) 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 $\gamma_{\text{TiO}_{1.5}}/\gamma_{\text{TiO}_2}$ ratio. However, in their experiments, the effect of alumina on the activity coefficient of TiO_x 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 $\text{TiO}_{1.5}$ and TiO_2 in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_x$ ladle type slags equilibrated with the $\text{Fe-C}_{\text{satd}}\text{-Ti(-Cr-Si)}$ or Fe-Al-Ti melts at 1 873 K.¹⁶⁾ The activity of $\text{TiO}_{1.5}$ 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 $[\text{Al}]\text{-(Al}_2\text{O}_3)$ equilibrium rather than by C-CO equilibrium. Even though Ariyo and Holappa also measured the activity of Ti_3O_5 (10 to 39 mass%) in the $\text{CaO-SiO}_2\text{-Ti}_3\text{O}_5$ slag system at 1 873 K,¹⁷⁾ there was no clear tendency for the effect of basicity on the thermodynamic behavior of $\text{TiO}_{1.67}$. In the later work,¹⁸⁾ they observed that the ratio of $\gamma_{\text{TiO}_{1.5}}$ to γ_{TiO_2} in the $\text{CaO-SiO}_2\text{-TiO}_x$ slag ($\text{CaO/SiO}_2=1.4$) shows a maximum at about 30 mass% TiO_x , as the concentration of TiO_x increases from 10 to 52 mass% at 1 873 K. This is relatively similar to the result measured by Tranell *et al.* However, the almost of TiO_x 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 $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_x$ slags has not been clarified yet.

Consequently, in the present work, the thermodynamic equilibrium between the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}_{\text{satd}}\text{-5mass\%CaF}_2\text{(-TiO}_x)$ slags and the $\text{Fe-11mass\%Cr}$ 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 $\text{Fe-11mass\%Cr-0.5mass\%Si-0.3mass\%Mn}$ steel. Alloys of about 730 g and the $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-5mass\%CaF}_2$ slags ($B=(\text{mass\% CaO}+\text{mass\% MgO})/(\text{mass\% SiO}_2)=1.6\text{--}5.8$) 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 in the premelted alloy were approximately less than 25 ppm.

The stainless steel reaction chamber, which was cooled by cooling water, was initially evacuated by the mechanical rotary pump and filled by Ar gas (1 atm) and followed by induction heating. The temperature was established to be 1 873 K using an R-type ($\text{Pt-13mass\%Rh/Pt}$) thermocouple and a proportional integral differential controller. Any possible interference of high frequency on temperature detecting was reduced by grounding the circuit of thermocouple. Preliminary trials confirmed that the RF interference was not significant in the present experimental setup and the temperature fluctuation of steel melts could be controlled within ± 3 K during experiments. The oxygen in Ar gas was removed by passing the gas through magnesium turnings heated to about 773 K, even though 5N (99.999%) purity Ar gas was used. After the steel samples were melted at

Fig. 1. Schematic diagram of the experimental apparatus.

1 873 K, the premelted slags were added and followed by the addition of aluminum and titanium equivalent to about 0.02 and 0.3 mass%, respectively. All of the additives such as slags and metals were dropped through the quartz tube under an inert atmosphere. Then, the system was equilibrated during about 60 min, which was determined by the preliminary experiments. That is, the concentration of MgO , SiO_2 , Al_2O_3 , and TiO_2 in the slag as well as titanium and aluminum in the steel melt showed a constant value within 40 min, approximately. Thus, it was confirmed that the slag was saturated by MgO . After equilibrating, the power of the furnace was turned off and the crucible assembly was quenched by helium gas, which was blown from the top surface of the crucible. A schematic diagram of the experimental apparatus is shown in Fig. 1.^{19–22)}

The metal and slag samples were prepared for chemical analysis. The content of major components such as chromium, silicon, manganese, and total aluminum were analyzed by an optical emission spectrometry and the content of dissolved aluminum and titanium was determined by the inductively coupled plasma spectroscope (ICP-AES, IRIS Advantage (REG), Thermo Electron, Waltham, MA). The content of oxygen was analyzed by fusion and the infrared absorption method after very careful preparation through an ultrasonic cleaning. The composition of the slag was analyzed by an X-ray fluorescence spectroscope (SRS3400, Bruker AXS, Cheshire, UK). The equilibrium compositions of metal and slag are listed in Table 1 and Table 2. Here, the presence of titanium oxide in the slag did not originate from initial addition but from slag-metal reactions that occur to achieve equilibrium. In the present study, the titanium oxide could be taken as mainly TiO_2 based on the previous studies by Tranell *et al.*,^{12–14)} Jung and Fruehan,¹⁶⁾ and Ariyo *et al.*,^{17,18)} because the oxygen partial pressure in the present study was in the order of $p_{\text{O}_2}=10^{-13}$ atm from the $[\text{Si}]\text{-(SiO}_2)$ and $[\text{Al}]\text{-(Al}_2\text{O}_3)$ equilibria.²²⁾

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.

Table 1. Equilibrium composition of the slags in the present study (mass%).

Run	CaO	Al ₂ O ₃	SiO ₂	TiO ₂	CaF ₂	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

[Cr]=11.1(±0.1)mass%, [Si]=0.51(±0.09)mass%, [Mn]=0.29(±0.01)mass%

$$[\text{Si}] + (\text{TiO}_2) = (\text{SiO}_2) + [\text{Ti}] \dots \dots \dots (1)$$

$$K_{(1)} = \frac{\gamma_{\text{SiO}_2} \times X_{\text{SiO}_2} \times a_{\text{Ti}}}{a_{\text{Si}} \times \gamma_{\text{TiO}_2} \times X_{\text{TiO}_2}} \dots \dots \dots (2)$$

$$\log a_{\text{Ti}} - \log X_{\text{TiO}_2} = \log a_{\text{Si}} - \log X_{\text{SiO}_2} + \log \frac{\gamma_{\text{TiO}_2}}{\gamma_{\text{SiO}_2}} + \log K_{(1)} \dots \dots \dots (3)$$

where $K_{(1)}$ is the equilibrium constant of Eq. (1), and γ_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 “ $\log a_{\text{Ti}} - \log X_{\text{TiO}_2}$ ” is in direct proportion to the “ $\log a_{\text{Si}} - \log X_{\text{SiO}_2}$ ” 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 “ $\log a_{\text{Ti}} - \log X_{\text{TiO}_2}$ ” and the “ $\log a_{\text{Si}} - \log X_{\text{SiO}_2}$ ” at 1873 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

Fig. 2. Relationship between $\log a_{\text{Ti}} - \log X_{\text{TiO}_2}$ and $\log a_{\text{Si}} - \log X_{\text{SiO}_2}$ at 1873 K.**Table 3.** Interaction parameters used in the present study.

e_i^j (r_i^j)	Cr	Si	Mn	Al	Ti	O
Al	0.030 ²⁷⁾	0.056	0.035 ²⁸⁾	0.043	0.016 ²⁹⁾	-1.98 ²⁵⁾ (39.82)
Ti	0.029 ³⁰⁾	-0.025 ³¹⁾	-0.043	0.024 ²⁹⁾	0.049 ³⁵⁾	-1.62 ³²⁾ (-0.36)
Si	-0.021 ²⁴⁾	0.10	-0.007*	0.058	-0.013*	-0.12
O	-0.032 ³³⁾	-0.066	-0.037 ³⁴⁾	-1.17 ²⁵⁾ (-0.010)	-0.54 ³²⁾ (0.039)	-0.17

* Calculated from the relation, $e_j^i = \frac{M_j}{M_i} e_i^j + 0.434 \times 10^{-2} \frac{M_i - M_j}{M_i} \dots^{23)}$

classical Wagner formalism using the first- and second-order interaction parameters, which are listed in **Table 3**.^{23–35)}

$$\log f_{\text{M}} = \sum_{i=\text{Cr, Si, Mn, Al, Ti, O}} (e_{\text{M}}^i \times [\text{mass\%}i] + r_{\text{M}}^i \times [\text{mass\%}i]^2) \dots \dots \dots (4)$$

where f_{M} , e and r 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.

$$K_{(5)} = \frac{\gamma_{\text{Al}_2\text{O}_3}^2 \times X_{\text{Al}_2\text{O}_3}^2 \times a_{\text{Ti}}^3}{a_{\text{Al}}^4 \times \gamma_{\text{TiO}_2}^3 \times X_{\text{TiO}_2}^3} \dots \dots \dots (6)$$

$$\begin{aligned} & 3 \log a_{\text{Ti}} - 3 \log X_{\text{TiO}_2} \\ &= 4 \log a_{\text{Al}} - 2 \log X_{\text{Al}_2\text{O}_3} + \log \frac{\gamma_{\text{TiO}_2}^3}{\gamma_{\text{Al}_2\text{O}_3}^2} + \log K_{(5)} \dots \dots \dots (7) \end{aligned}$$

Figure 3 exhibits a relationship between “ $3 \log a_{\text{Ti}} - 3 \log X_{\text{TiO}_2}$ ” and “ $4 \log a_{\text{Al}} - 2 \log X_{\text{Al}_2\text{O}_3}$ ” at 1873 K, where a good linear relationship ($r^2=0.90$) between them is ob-

Fig. 3. Relationship between $3 \log a_{\text{Ti}} - 3 \log X_{\text{TiO}_2}$ and $4 \log a_{\text{Al}} - 2 \log X_{\text{Al}_2\text{O}_3}$ at 1873 K.

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)+(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 Holappa^{17,18)} 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)}

$$\Delta G^\circ = -659880 + 229T \quad (\text{J/mol}) \dots \dots \dots (9)$$

$$\log \gamma_{\text{TiO}_2} = \log a_{\text{Ti}} + 2 \log a_{\text{O}} + K_{(8)} - \log X_{\text{TiO}_2} \dots \dots \dots (10)$$

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 $\log B$, which is on the extended line estimated by Ito and Sano. The activity coefficient of Ti_3O_5 ($\log \gamma_{\text{Ti}_3\text{O}_5}$) 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 $\log B = 0.7$ 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_2O_3 and to 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 $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ (silica > 50 mass%) glasses could be a network modifier in the form of $[\text{TiO}_6]$ -octahedron at high temperatures, whereas it becomes a network former in the form of $[\text{TiO}_4]$ -tetrahedron at low tem-

Fig. 4. Basicity dependence of the activity coefficient of TiO_2 (and Ti_2O_3 and Ti_3O_5) in various slags.

peratures 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 $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}$ ($B=0.8$ 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 $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ ($B=1.0$) 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 γ_{TiO_2} as shown in Morizane *et al.*'s paper. They calculated the γ_{TiO_2} using the equilibrium constant of the TiO_2-C equilibrium reaction ($\text{TiO}_2(\text{s}) + \text{C}(\text{s}) = \text{Ti}(\text{1 wt\%}) + \text{CO}(\text{g})$; Eq. (20) in Ref. 15)) and the Henrian activity coefficient of titanium (f_{Ti}) in carbon saturated iron. They used the value of $f_{\text{Ti}} = 0.023$ 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% SiO_2)+(mass% Al_2O_3) ($=S/(S+A)$). This indicates that the attraction between TiO_2 and SiO_2 is greater than that between TiO_2 and Al_2O_3 in the present slag system, which could be expected from the electronegativity difference between each cation involved ($\epsilon_{\text{Ti}} = 1.5$, $\epsilon_{\text{Si}} = 1.8$, $\epsilon_{\text{Al}} = 1.5$)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

Fig. 5. Effect of (mass% SiO₂)/(mass% SiO₂+mass% Al₂O₃) ratio on the activity coefficient of TiO₂ in the CaO–SiO₂–Al₂O₃–MgO_{satd}–CaF₂ slags at 1873 K.

Fig. 6. Effect of TiO₂ concentration on the activity coefficient of TiO₂ in the CaO–SiO₂–Al₂O₃–MgO_{satd}–CaF₂ slags at 1873 K.

about 0.6. Tranell *et al.*^{12–14)} suggested that the complex behavior of titanium oxide, which shows a minimum Ti^{3+}/Ti^{4+} or maximum $\gamma_{TiO_{1.5}}/\gamma_{TiO_2}$ ratio as a function of TiO_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_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 SiO₂ and TiO₂ concentrations, the conclusive remarks for the effect of TiO₂ concentration on the stability of titanate anion complexes are still remained for further discussion.

The activity of TiO₂ is shown in **Fig. 7** as a function of TiO₂ concentration in the slags at 1873 K. The measured results by Morizane *et al.*,¹⁵⁾ Jung and Fruehan,¹⁶⁾ and Ariyo and Holappa^{17,18)} are compared to the present value. The activity of TiO₂ in the CaO–SiO₂–Al₂O₃–10 mass% MgO TiO_x system measured by Moriazne *et al.* at 1773 K is extrapolated to 1873 K based on the regular solution assumption for comparison. The activity of TiO₂ in this slag system shows a negative deviation from an ideality, while that in the CaO–SiO₂–Al₂O₃–MgO_{satd}–(CaF₂) system measured by Jung and Fruehan, and by the present authors is relatively close to the ideal behavior up to about $X_{TiO_2}=0.1$. This is mainly due to the basic characteristic of TiO₂ as discussed previously in Fig. 4. Also, the activity of Ti₃O₅ measured by

Fig. 7. Activity–mole fraction relationship of TiO₂ in various slags at 1873 K.

Ariyo and Holappa qualitatively follows the Raoult's law at high TiO₂ concentration region.

In summary, the present slag–metal equilibrium experiments could provide the useful information regarding the thermodynamic behavior of TiO₂ in the slags and especially the effect of slag composition on it. The TiO₂ 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 aluminate base melts used in secondary refining processes. However, the effect of TiO₂ concentration on the stability of TiO₂ in the slag is still in a room for further discussion including structural studies.

4. Conclusions

The thermodynamic equilibrium between the CaO–SiO₂–Al₂O₃–MgO_{satd}–CaF₂–(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 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 $\log \gamma_{TiO_2}$ increases by increasing the $\log B$, which is on the extended line estimated by Ito and Sano. By combining this with the previous results, in multi component calcium(–magnesium) silicate slags containing 5 to 30 mass% Al₂O₃ and to about 15 mass% TiO₂, the TiO₂ 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.

(3) The $\log \gamma_{TiO_2}$ gradually decrease by increasing the ratio of (mass% SiO₂) to (mass% SiO₂)+(mass% Al₂O₃), indicating that the attraction between TiO₂ and SiO₂ is greater than that between TiO₂ and Al₂O₃ in the present slag system. This could be explained from the electronegativity difference between each cation involved.

(4) The activity of TiO₂ in the slag system containing 10 mass% MgO shows a negative deviation from an ideal-

ity, while that in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}_{\text{satd}}(-\text{CaF}_2)$ system is relatively close to the ideal behavior up to about $X_{\text{TiO}_2}=0.1$. This is mainly due to the relatively basic characteristic of TiO_2 .

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