Thermodynamics of the Al$_2$O$_3$–SiO$_2$–TiOX Oxide System at 1873 K

Mitsuhiko OHTA and Kazuki MORITA

Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656 Japan.

(Received on October 25, 2001; accepted in final form on January 25, 2002)

Isothermal phase relations for the Al$_2$O$_3$–SiO$_2$–TiOX system have been investigated under strongly reducing conditions, achieved by equilibrium between graphite and CO gas, $P_{O_2}=4.56 \times 10^{-16}$ atm at 1873 K, in equilibria with a saturating oxide tablet.

Activities of Al$_2$O$_3$ and SiO$_2$ were measured by the Knudsen effusion method. Activities of SiO$_2$ were also measured by the chemical equilibrium between the oxide and the Fe–Si–C alloy. Activity of TiOX was also estimated from the composition of the Si–Al–Ti alloy in equilibrium with the oxide assuming that the alloy conformed to a regular solution. In addition, steel composition equilibrated with the oxide of arbitrary composition has been calculated by the activities of each component of the oxide system obtained in the present study.

KEY WORDS: oxide metallurgy; inclusion; phase diagram; activity measurement; Knudsen effusion method.

1. Introduction

Inclusions in steels have been considered to be harmful to quality of final product of steels, and extensive studies on removal of inclusions or making them harmless, have been mostly concentrated. Al$_2$O$_3$ formed by aluminum deoxidation in a secondary steel refining process is known to cause a defect like a flaw and a crack. Therefore, a substitution of simple deoxidation of aluminum is required.

On the other hand, an innovative attempt called “oxide metallurgy” has been made to improve steel properties by controlling the size, composition and distribution of non-metallic inclusions in steels. In such a process, an appropriate oxide will act as a precipitation site of MnS that is a transformation site of intragranular ferrite from austenite. If the oxides were finely dispersed in steels, MnS formed on the oxide should make the ferrite grains so fine that the toughness of steels could be enhanced. Sawai et al. have reported that the complex deoxidization by strong and weak deoxidizing agents is effective for the fine dispersion of deoxidation product, and they have also reported that an oxide with high sulfide capacity was preferable for MnS precipitation. Moreover, Ogibayashi reported that low liquidus temperature of the oxide would promote the MnS precipitation.

Thus, thermodynamic properties of the oxide inclusions in steels must be investigated in order to optimize the processes concerned with the inclusions. Some thermodynamic studies of oxide systems satisfying the conditions mentioned above have been done.

Amitani et al. investigated the phase relations for the MnO–SiO$_2$–TiO$_2$ system at 1573 K and 1773 K. Ito et al. measured the activity of MnO and sulfide capacity for the MnO–SiO$_2$–TiO$_2$ system at 1673 K. Authors have investigated phase relations and activities of each component for the MnO–Al$_2$O$_3$–TiO$_2$ system at 1673 K and 1873 K. According to these studies, the compositions of low liquidus temperature and high sulfide capacity for the oxide system including MnO and TiO$_2$ have been obtained. Moreover, steel compositions equilibrated with the oxide have been calculated with the activity data.

However, in the practical process, TiO$_2$ is not the equilibrium state as titanium oxide because of the low partial pressure of oxygen. Ti$^{3+}$ and Ti$^{4+}$ are reported to coexist in a melt of the oxide under the strongly reducing condition. In addition, aluminum is the strong deoxidant enough to reduce MnO in the oxide phase. Therefore, the Al$_2$O$_3$–SiO$_2$–TiOX oxide system will be formed as deoxidation product in secondary refining process practically.

In this paper, phase relations of the Al$_2$O$_3$–SiO$_2$–TiOX system as well as the activities of Al$_2$O$_3$ and SiO$_2$ have been investigated at 1873 K. Also, the steel composition equilibrated with the oxide has been calculated.

2. Experimental Method

2.1. Measurement of the Phase Relations

A MoSi$_2$ electric resistance furnace connected to a proportional integral differential (PID) controller with a Pt/6%Rh–Pt/30%Rh thermocouple was used for all the experiments in the present study. Temperature was controlled at 1873 ± 1 K over a length of 50 mm in a mullite tube settled in the furnace. A graphite crucible with 4 g of the Al$_2$O$_3$–SiO$_2$–TiOX oxide and a tablet of the saturating oxide was placed in the furnace for 24 h. After the experiment, the crucible was taken out of the furnace and cooled by argon flush. The molten oxide phase was separated from the tablet, broken and ground into fine powder, and was subjected to chemical analysis. Silicon in the oxide was determined by the gravimetry, aluminum and total titanium con-
Activities of Al$_2$O$_3$ and SiO$_2$ in the oxide and alloy were represented as following equations.

$$\text{SiO}(g) = 1/2 \text{Si}(l) + 1/2 \text{SiO}_2(s, \text{cryst}) \quad .......(3)$$

$$K_3 = \frac{a_{\text{Si}}^{1/2} \cdot a_{\text{SiO}}^{1/2}}{P_{\text{CO}}}$$

$$\text{AlO}(g) = 1/3 \text{Al}(l) + 1/2 \text{AlO}_3(s) \quad .......(4)$$

$$K_4 = \frac{a_{\text{Al}}^{1/2} \cdot a_{\text{AlO}}^{1/3}}{P_{\text{Si}}}$$

Therefore, activities of Al$_2$O$_3$ and SiO$_2$ were obtained by the following equations.

$$a_{\text{SiO}} = \frac{K_3^3 \cdot P_{\text{SiO}}^3}{P_{\text{Si}}^3} \quad .......(5)$$

$$a_{\text{AlO}} = \frac{K_4^3 \cdot P_{\text{AlO}}^3}{P_{\text{Al}}^3} \quad .......(6)$$

where $P_i$ represents a partial pressure of component $i$ and $P^\circ_i$ is a partial pressure of i component of standard state.

On the other hand, relationship between the ion current and the partial pressure of the component $i$ was represented as follows.

$$P_i = k_i \cdot I_i \cdot T \quad .......(7)$$

where $P_i$ is a partial pressure of $i$ component, $k_i$ is the apparatus constant including the ionization cross section of $i$ species, and $T$ is temperature.

In the present study, the apparatus constant was determined as follows. Al$_8$Si$_2$O$_{13}$, Al$_2$O$_3$, and the Al–Si alloy were equilibrated in the BN crucible and the ion current values were monitored which corresponds to Al, Si, AlO, and SiO by mass spectrometer. Equilibrium among Al$_8$Si$_2$O$_{13}$, Al$_2$O$_3$, Al and Si is represented as follows.

$$\Delta G^\circ = 138 600 - 23.89 T \quad (J/mol)^8$$

Activities of Al$_8$Si$_2$O$_{13}$ and Al$_2$O$_3$ are unity and that of silicon is almost unity because compositions of other components are very low. That of aluminum is calculated to 1.8×10$^{-3}$ with the Gibbs energy change of Eq. (8). Thus, activities of all components in Eqs. (3) and (4), and the apparatus constants of respective components could be obtained by measurement of ion current.

Preliminarily, the measurement for ion current corre-

tent by ICP-AES, and trivalent titanium content by a titration of potassium dichromate. X-ray diffraction analysis was done on the boundary between the oxide and the tablet to confirm the solid phase in equilibrium. Analytic condition is shown in Table 1.

### 2.2. Activity Measurement by the Equilibrium between the Oxide and the Fe–Si–C Alloy

A graphite crucible or SiC crucible with 4 g of the oxide and 10 g of the Fe–Si–C alloy was placed in the furnace at 1 873 K for more than 48 h. Carbon monoxide gas was flown into the furnace to maintain $P_{\text{CO}}=1.013 \times 10^5$ Pa. After the experiment, the specimen was taken out of the furnace and cooled by argon flush. Both phases were separated into the oxide and the alloy, and the composition of the oxide was measured by chemical analyses. Silicon in the alloy was measured by the gravimetry method. Carbon content in the alloy was measured by LECO combustion analyzer. The composition of the oxide and the alloy were put into a BN crucible covered by a BN lid with an orifice of 0.2 mm in diameter. The crucible was settled in the center of the furnace heated by tantalum heating elements at 1 873 K. Ion current was monitored which corresponds to Al, Si, AlO, and SiO, respectively.

<table>
<thead>
<tr>
<th>Table 1. Conditions of X-ray diffraction analyses.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tube voltage</td>
</tr>
<tr>
<td>Tube current</td>
</tr>
<tr>
<td>Step</td>
</tr>
<tr>
<td>Scanning rate</td>
</tr>
<tr>
<td>Source</td>
</tr>
<tr>
<td>Divergence slit</td>
</tr>
<tr>
<td>Scatter slit</td>
</tr>
<tr>
<td>Receiving slit</td>
</tr>
</tbody>
</table>

X-ray diffraction analysis of potassium dichromate. X-ray diffraction analysis was done on the boundary between the oxide and the tablet to confirm the solid phase in equilibrium. Analytic condition is shown in Table 1.

### 2.3. Activity Measurement by Knudsen Effusion Method

The Knudsen effusion method was employed to measure activities of Al$_2$O$_3$ and SiO$_2$. The Al$_2$O$_3$–SiO$_2$–TiO$_2$ oxide and the Al–Si–Ti alloy were equilibrated in a graphite crucible for more than 48 h under $P_{\text{CO}}=1.013 \times 10^5$ Pa at 1 873 K, then subjected to chemical analyses. About 0.1 g of the oxide and the alloy were put into a BN crucible covered by a BN lid with an orifice of 0.2 mm in diameter. The crucible was settled in the center of the furnace heated by tantalum heating elements at 1 873 K. Ion current was measured regarding the molecular weight of 27, 28, 43 and 44 by a quadrupole mass spectrometer. The molecular weight of 27, 28, 43 and 44 correspond to Al, Si, AIO and SiO, respectively.

Equilibria between Al$_2$O$_3$ and SiO$_2$ in the oxide and aluminum and silicon in the alloy are represented as following equations.

$$\text{SiO}(g) = 1/2 \text{Si}(l) + 1/2 \text{SiO}_2(s, \text{cryst}) \quad .......(3)$$

$$K_3 = \frac{a_{\text{Si}}^{1/2} \cdot a_{\text{SiO}}^{1/2}}{P_{\text{CO}}}$$

$$\text{AlO}(g) = 1/3 \text{Al}(l) + 1/2 \text{AlO}_3(s) \quad .......(4)$$

$$K_4 = \frac{a_{\text{Al}}^{1/2} \cdot a_{\text{AlO}}^{1/3}}{P_{\text{Si}}}$$

Therefore, activities of Al$_2$O$_3$ and SiO$_2$ were obtained by the following equations.

$$a_{\text{SiO}} = \frac{K_3^3 \cdot P_{\text{SiO}}^3}{P_{\text{Si}}^3} \quad .......(5)$$

$$a_{\text{AlO}} = \frac{K_4^3 \cdot P_{\text{AlO}}^3}{P_{\text{Al}}^3} \quad .......(6)$$

where $P_i$ represents a partial pressure of component $i$ and $P^\circ_i$ is a partial pressure of $i$ component of standard state.

On the other hand, relationship between the ion current and the partial pressure of the component $i$ was represented as follows.

$$P_i = k_i \cdot I_i \cdot T \quad .......(7)$$

where $P_i$ is a partial pressure of $i$ component, $k_i$ is the apparatus constant including the ionization cross section of $i$ species, and $T$ is temperature.

In the present study, the apparatus constant was determined as follows. Al$_8$Si$_2$O$_{13}$, Al$_2$O$_3$, and the Al–Si alloy were equilibrated in the BN crucible and the ion current values were monitored which corresponds to Al, Si, AlO, and SiO by mass spectrometer. Equilibrium among Al$_8$Si$_2$O$_{13}$, Al$_2$O$_3$, Al, and Si is represented as follows.

$$\Delta G^\circ = 138 600 - 23.89 T \quad (J/mol)^8$$

Activities of Al$_8$Si$_2$O$_{13}$ and Al$_2$O$_3$ are unity and that of silicon is almost unity because compositions of other components are very low. That of aluminum is calculated to 1.8×10$^{-3}$ with the Gibbs energy change of Eq. (8). Thus, activities of all components in Eqs. (3) and (4), and the apparatus constants of respective components could be obtained by measurement of ion current.

Preliminarily, the measurement for ion current corre-
sponding to Si and SiO under the equilibrium between Si and SiO2 were repeated. As a result, changes of apparatus constant for Si and SiO were within 10%. In the derivation of activities, it was assumed that the constant would not change between the preliminary measurement for the constant determination and the practical measurement.

3. Results and Discussion

3.1. Phase Relations for the Al2O3–Ti2O3 Binary System at 1 873 K

Phase diagram of the Al2O3–Ti2O3 system have been reported in a literature as shown in Fig. 1.9) However, details about solid solubility were incomplete. On the other hand, the Al2O3–TiO2 system obtained in air is known to have intermediate compound, Al2O3·TiO2.9) Thus, phase relations for the Al2O3–Ti2O3 binary system were investigated in prior to those for the Al2O3–SiO2–TiO2 system.

A mixture of the 50mass%Al2O3–50mass%Ti2O3 powder was pressed and shaped into a tablet. The tablet was sintered under the same condition as the measurement of phase relations for the Al2O3–TiO2–SiO2 system mentioned in Sec. 2.1. This sample was analyzed by X-ray diffraction (XRD). The XRD pattern of the sintered specimen compared with the simply mixed powder is shown in Fig. 2. It is found that there is no intermediate compound in the Al2O3–Ti2O3 binary system according to the diffraction spectra. Since Al2O3 and Ti2O3 have the same crystal structure, the reciprocal solid solubilities of Al2O3 and Ti2O3 can be obtained from the shift of spectra based on the following equation assuming that the lattice spacing has a linear relation with the solid solubility.

\[
x = \frac{(d_{TiO_2} - d_{AlO_2})}{(d_{TiO_2} - d_{AlO_2})} \quad \text{................. (9)}
\]

where \(x\) denotes solid solubility described as the molar fraction of Al2O3 in Ti2O3 solid phase and \(d\) is the lattice spacing. The molar fraction of Ti2O3 in Al2O3 can be also obtained by the same way. There is an error more than 2% as the dependence on the accuracy of measurement of the lattice spacing in this way.

Measurements were done on (220), (306) and (0210) planes and the average values of these inter-planar distances were calculated. Results of these measurements and calculation are shown in Table 2, where the results of practical measurements on the raw mixture of Al2O3 and Ti2O3 are adopted as values of \(d_{0}\). According to the results, solid solubility of Al2O3 into Ti2O3 is 3.6 mass% and that of Ti2O3 into Al2O3 is 6.2 mass%. Thus, Al2O3 and Ti2O3 will coexist with those reciprocal solubilities although these solid solubilities are smaller than those deduced from Fig. 1.

3.2. Phase Relations for the Al2O3–SiO2–TiO2 System at 1 873 K

The results of the measurement of the Al2O3–SiO2–TiO2 system at 1 873 K are shown in Table 3. All the equilibrium compositions were obtained by more than twice experiments as mentioned Sec. 2.1. For instance, change of experimental composition for the 15.79mass%Al2O3–67.36mass%SiO2–16.85mass%TiO2 is shown in Fig. 3. Isothermal phase diagram of the Al2O3–SiO2–TiO2 system at 1 873 K is shown in Fig. 4. Liquidus of the Al2O3–SiO2–TiO2 investigated in air is also shown by broken line in Fig. 4. In this study, species of TiO2 equilibrated with liquid phase was observed to be Ti2O3, which is consistent with the results of Amitani et al.4) As mentioned in the previous section, Al2O3 and Ti2O3 coexist with the reciprocal
solubilities, so the pure Al$_2$O$_3$ and Ti$_2$O$_3$ may not be in equilibrium with the liquid. Hence, the tie lines around the Al$_2$O$_3$ and the Ti$_2$O$_3$ corners are drawn as broken ones in this figure for convenience.

Maximum solubility of Al$_2$O$_3$ is 28 mass% and that of TiO$_x$ is 50 mass%. Liquid area of the Al$_2$O$_3$–SiO$_2$–TiO$_x$ system is narrow compared with the Al$_2$O$_3$–SiO$_2$–TiO$_2$ system in the region of the lower SiO$_2$ content. This difference is similar to that between the MnO–SiO$_2$–TiO$_x$ and the MnO–SiO$_2$–TiO$_2$ systems.\(^4\)

### 3.3. Liquidus for the Al$_2$O$_3$–SiO$_2$–TiO$_x$–5mass%MnO System

In order to investigate the effect of MnO considerably contained in the originally formed oxide, the doubly saturated compositions of each component in the Al$_2$O$_3$–SiO$_2$–TiO$_x$–MnO system were determined. Initial amount of MnO addition was 5 mass% into the Al$_2$O$_3$–SiO$_2$–TiO$_x$ oxide. Equilibrium composition obtained in these measurements is shown in Table 4. Final MnO contents were fluctuated from 3.7 mass% to 5.4 mass%. Deduced liquidus of that system is shown in Fig. 5. Liquidus is drawn as the pseudo-ternary system without MnO content. Addition of a small amount of MnO enlarges the liquidus area of the Al$_2$O$_3$–SiO$_2$–TiO$_x$ system. Thus, it is found that liquidus would be shrinking with reducing MnO in the practical process.

### 3.4. Behavior of Trivalent and Tetravalent Titanium in the Oxide Melts

The dependence of valence of titanium on the composition of the melts has been investigated along the composition of (mass% Al$_2$O$_3$)/(mass% TiO$_x$) \(\approx 0.67\). Relationship between Ti$^{4+}$/Ti$^{3+}$ ratio and SiO$_2$ content in the oxide is shown in Fig. 6. Ti$^{4+}$/Ti$^{3+}$ ratio increases with SiO$_2$ content, which suggests that TiO$_x$ is more acidic than TiO$_2$. This tendency is inconsistent with the MnO–SiO$_2$–TiO$_2$ system by Amitani \textit{et al.} and the CaO–SiO$_2$–Al$_2$O$_3$–TiO$_2$ system by Ito \textit{et al.}.\(^{10}\) They have concluded that tetravalent titanium is more acidic than trivalent one in the oxide melt.
In the MnO–SiO$_2$–TiO$_X$ system with higher basicity than the Al$_2$O$_3$–SiO$_2$–TiO$_X$ system, red-ox equilibrium of Ti in such oxide is considered as follows.

$$\text{Tetravalent titanium forms structure unit of complex anion like TiO}_3^{2-}. \text{This anion is decomposed into single trivalent titanium as partial pressure of oxygen decreased or basicity of the melt decreased.}$$

On the other hand, relationship between Ti$^{4+}$/Ti$^{3+}$ ratio and TiO$_X$ content along the composition of (mass% Al$_2$O$_3$)/(mass% TiO$_X$)»0.28 is shown in Fig. 7. Ti$^{4+}$/Ti$^{3+}$ ratio increases with TiO$_X$ content. Thus, it is found that TiO$_X$ as well as SiO$_2$ influenced Ti$^{4+}$/Ti$^{3+}$ ratio.

In order to examine the contradiction between the present work and others, structure of some samples was investigated by the Raman spectrometry. Conditions for the measurements are shown in Table 5 and Raman spectra are shown in Fig. 8. According to the results, although relative intensities are weak, only 1 600 cm$^{-1}$ band corresponding to 3-D network is observed while other band peaks corresponding to structure of broken network of silica such like monomer, dimer, chain and sheet are hardly recognized. Thus, Al$_2$O$_3$ and Ti$_2$O$_3$ do not seem to behave as network-modifiers, but may be incorporated in silicate network structures. Then, ratio of intensity of 1 600 cm$^{-1}$ peak and that around 1100 cm$^{-1}$ corresponding to the structure of sheet of silica were investigated as an index of breakage of network structure. Dependence of the ratio of intensities upon the oxygen partial pressure is shown in Fig. 9. Relative intensity of 1 600 cm$^{-1}$ decreases with the decrease of oxygen partial pressure. On the other hand, relative intensity of 1 600 cm$^{-1}$ decreases as SiO$_2$ content decreases compared between T1 and T5 with the same oxygen partial pressure. According to the tendency, it seems that tetravalent titanium ions form the network structure with silicon and oxygen described as Fig. 10, schematically. Both of the tetravalent and trivalent titanium form the complex structure with oxygen and silicon. 3-D network of Si–Ti–O including tetravalent titanium is partially broken into the network including non-bonding oxygen as oxygen partial pressure decreases or basicity of the melt increases.
3.5. Activities of AlO1.5 and SiO2 in the Al2O3–SiO2–TiOX System

Activities of AlO1.5 and SiO2 obtained by the chemical equilibrium between the oxide and the Fe–Si–C alloy and those by Knudsen effusion method are shown in Fig. 11 and Table 6. Activities of SiO2 measured by both methods are in good agreement. For instance, activity value of SiO2 of the composition doubly saturated with Al2O3 and Al6Si2O13 is obtained to be 0.45 by the chemical equilibrium and 0.46 by Knudsen effusion method while it is calculated to be 0.462 by the standard free energy of formation of Al6Si2O13. Thus, the results of activity measurement of AlO1.5 by Knudsen effusion method also seem to be reasonable.

When SiO2 replaces TiOX from (mass% SiO2) 5 to 75 along the composition of (mass% Al2O3) 5 to 15, activity of AlO1.5 drops near the liquidus of saturated by Al2O3, then decreases gradually from 0.66 to 0.57. This phenomenon seemed to reflect that both of the SiO2 and TiOX behave as network-former in the melts mentioned in the previous section.

3.6. Estimation of TiOX Activity from the Composition and Activity of Each Component of the Si–Al–Ti Alloy in Equilibrium with the Oxide Melt

Composition of the Si–Al–Ti alloy equilibrated with the oxide melt in some of the activity measurements was determined assuming that composition of alloy did not change during the measurement by the Knudsen cell. The activity of each component of the alloy can be calculated from the composition by Toop’s method11) described as follows when the Si–Al–Ti alloy behaves as a regular solution.

$$\log \gamma_{2(1-2-3)} = \frac{G^G_{1,3}}{19.1447 \log \left(\frac{1-N_2}{N_2} \frac{1-N_3}{N_3} \frac{1-N_{TiOx}}{N_{TiOx}}\right)}$$

where subscripts of 1–2–3, 1–2 and 2–3 denote the ternary of 1–2–3, the binary of 1–2 and that of 2–3, respectively. G\textsuperscript{G} represents excess free energy. In the method, activity coefficient of component 2 in ternary system can be calculated with activity coefficients of 2 in two binary systems and excess free energy of the other binary system. $\gamma_{2(1-2-3)}$ and $\gamma_{3(1-2-3)}$ can be derived in the same way. In the present analysis, the data reported by Desai12) are adopted as the thermodynamic property of the Al–Si and the Al–Ti and those by Miki et al.13) for the Si–Ti binary system, respectively.

Composition and activities of each component in the Si–Al–Ti alloy equilibrated with the oxide are shown in Table 7. Oxygen partial pressure in the system can be determined by the equilibrium between SiO2 in the oxide and silicon in the alloy. Activities of TiO1.5 and TiO2 are calculated from the oxygen partial pressure, activity of titanium in the alloy and standard free energies of formation of TiO1.5 and TiO2.14) These results are shown in Fig. 12. This figure shows also activities of TiO1.5 and TiO2 in the Ti2O3 saturated point.

When the content of SiO2 increases from 55 mass% to 80 mass% along the composition of (mass% Al2O3) / (mass% TiO2) = 0.43, activity coefficient of TiO2 changes

![Fig. 10. Schematic image of structure of the Si–Ti–O in the oxide melt.](image)

![Fig. 11. Activities of SiO2 and AlO1.5 in the Al2O3–SiO2–TiOX system at 1873 K.](image)

<p>| Table 6. Activities of SiO2 and AlO1.5 in the Al2O3–SiO2–TiOX system at 1873 K. |
|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition of the oxide (mass%)</th>
<th>$a_{AlO1.5}$</th>
<th>$a_{SiO2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>301</td>
<td>16.3</td>
<td>56.8</td>
<td>26.9</td>
</tr>
<tr>
<td>302</td>
<td>22.8</td>
<td>51.5</td>
<td>25.7</td>
</tr>
<tr>
<td>303</td>
<td>12.8</td>
<td>43.0</td>
<td>44.2</td>
</tr>
<tr>
<td>304</td>
<td>17.1</td>
<td>74.9</td>
<td>8.0</td>
</tr>
<tr>
<td>305</td>
<td>21.1</td>
<td>60.5</td>
<td>18.4</td>
</tr>
<tr>
<td>306</td>
<td>12.8</td>
<td>80.6</td>
<td>6.6</td>
</tr>
<tr>
<td>307</td>
<td>8.8</td>
<td>85.4</td>
<td>6.2</td>
</tr>
</tbody>
</table>

© 2002 ISIJ

479
from 0.04 to 0.13 while that of TiO\textsubscript{1.5} increases from 3.9 to 29, and ratio of \( \frac{\gamma_{\text{TiO}}}{\gamma_{\text{TiO}_{1.5}}} \) changes from 1.03\textsuperscript{3}10\textsuperscript{2} to 1.45\textsuperscript{3}10\textsuperscript{2}. The phenomenon that TiO\textsubscript{2} is more stable than TiO\textsubscript{1.5} with lower basicity is in agreement with the structural model described in Sec. 3.4.

### 3.7. Calculation of the Steel Composition in Equilibrium with the Oxide

Steel composition equilibrated with the oxide of arbitrary composition can be calculated using the data obtained in the present work. Deoxidation equilibrium about metal component, M in the steel is represented as follows.

\[
\text{mM} = \text{nO} = \text{M}_i\text{O}_n(s) \quad (M: \text{Al, Si and Ti}) \quad \ldots(12)
\]

\[
\log K = \log a_{\text{M}_i\text{O}_n} - m \log f_{\text{M}_i} - n \log\text{mass}\%\text{O} \quad \ldots(13)
\]

\[
\log f_{\text{M}_i} = \sum_j \epsilon_{\text{M}_i}^j \text{mass}\%\text{M}_j + \epsilon_{\text{O}}^\text{O} \text{mass}\%\text{O} \quad \ldots(14)
\]

where \( f_{\text{M}_i} \) is activity coefficient of \( M_i \) in referred to 1 mass\% of \( M_i \) and \( \epsilon_i^j \) is an interaction parameter between \( i \) and \( j \) in the steel, respectively. Interaction parameters used in the calculation are shown in Table 8.

Calculation was done along \( \frac{\text{mass}\%\text{Al}_2\text{O}_3}{\text{mass}\%\text{TiO}_{X}} \approx 0.43 \). Oxygen content was assumed to be 30 mass ppm in the steel and Eq. (13) was solved about contents of aluminum, silicon and titanium by trial and error. Relationship between the composition of the oxide and the steel is shown in Fig. 13.

![Fig. 13](image)

Figure 13 shows a considerable change in titanium content of the steel with the change in \( \frac{\text{mass}\%\text{Al}_2\text{O}_3}{\text{mass}\%\text{TiO}_{X}} \) slightly changes. Titanium content in the steel changes from 0.024 mass ppm to 44.6 mass ppm while silicon content from 2.2 mass\% to 0.57 mass\% when SiO\textsubscript{2} content of the oxide increases from 47 mass\% to 78 mass\%. It is considered that the remarkably large value of the interaction parameter between silicon and titanium in the steel has caused such estimation. Therefore, these parameters must be examined intensively. On the other hand, aluminum content is in the range from 7 mass ppm to 10 mass ppm when the steel is in equilibrium with the melting oxide. An effect of complex deoxidation of the Al–Si–Ti is hardly recognized compared with value for single deoxidation of Al, 10 mass ppm.\textsuperscript{15)}

### 4. Conclusions

Thermodynamic properties of the \( \text{Al}_2\text{O}_3\text{–SiO}_2\text{–TiO}_{X} \) sys-
tem at 1873 K have been investigated in order to optimize the process related to the oxide inclusions.

- Reciprocal solid solubility for the Al₂O₃–Ti₂O₃ binary system was investigated by X-ray diffraction. Al₂O₃ and Ti₂O₃ coexist with solid solubility of 3.6 mass% Al₂O₃ into Ti₂O₃ and that of 6.2 mass% Ti₂O₃ into Al₂O₃.
- Phase relations of the oxide system were measured by the chemical equilibrium between the oxide and the tablet of the saturating oxide. Liquidus area is narrower than that of the Al₂O₃–SiO₂–TiO₂ system in the region of lower SiO₂ content.
- Liquidus for the Al₂O₃–SiO₂–TiO₂–5mass%MnO system was investigated. Liquidus changes wider with addition of MnO.
- Behavior of tetravalent and trivalent titanium was investigated about relationship between the ratio of Ti⁴⁺/Ti³⁺ and SiO₂ content. Phenomenon that TiO₂ is more stable than TiO₁.₅ in high SiO₂ content is explained by the structural model of the Si–Ti–O in the oxide melt.
- Activities of AlO₁.₅ and SiO₂ were measured by the chemical equilibrium between the oxide and the Fe–Si–C alloy and Knudsen effusion method. Activities of SiO₂ obtained by the both methods have good agreement with each other.
- Activities of TiO₂ and TiO₁.₅ were calculated from the activity of the Si–Al–Ti alloy estimated from the composition by Toop’s method.
- Steel composition in equilibrium with the oxide was calculated with the interaction parameter in the steel and the activities of AlO₁.₅, SiO₂ and TiO₁.₅. Though activity of TiO₁.₅ changes slightly, titanium content changes remarkably with the change of content of Al₂O₃ and SiO₂.

Acknowledgements

This research has been done as a part of Grant-in-Aid for scientific research program 13650800.

The authors are grateful to Nippon Steel Corporation for financial support, and Prof. Ishii and Dr. Sasaki, Hokkaido University, for their help in the measurement of Raman spectroscopy.

REFERENCES