Thermodynamic Modeling of the Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ System and Its Applications to the Fe–Al–Ti–O Inclusion Diagram

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All available thermodynamic and phase diagram data have been critically evaluated and optimized for the liquid slag phase and for all solid phases at 1 bar pressure from 298 K to above the liquidus temperatures for the systems Al$_2$O$_3$–TiO$_2$, Al$_2$O$_3$–Ti$_2$O$_3$, and Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$, and a database of model parameters has been prepared. The Modified Quasichemical Model was employed for the molten oxide phase. The thermodynamic modeling predicts the existence of a liquid oxide Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ phase at secondary steelmaking conditions. The database was used to calculate the inclusion diagram for Al–Ti deoxidation at 1 600°C.

KEY WORDS: thermodynamic modeling; Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$; Al–Ti deoxidation; inclusion; FactSage.

1. Introduction

The Fe–Al–Ti–O inclusion diagram has been investigated\(^1\)–\(^4\) with a view to understanding the formation of oxide inclusions and nozzle clogging for Ti-bearing Al-killed steels. However, discrepancies still remain. Ruby-Meyer \textit{et al.}\(^1\) presented an inclusion diagram for Al/H$_2$O1 Ti complex deoxidation of Fe–0.1%Mn–0.03%Si–Al–Ti–O steel at 1 580°C. The proposed inclusion diagram showed a liquid Al$_2$O$_3$–TiO$_2$ oxide phase as well as solid Al$_2$O$_3$ and Ti$_2$O$_3$ phases. These authors reported that liquid Al$_2$O$_3$–TiO$_2$ inclusions were observed in deoxidation experiments. Later, Jung \textit{et al.}\(^2\) presented a calculated inclusion diagram for Al/H$_2$O1 Ti complex deoxidation at 1 600°C which showed only solid Al$_2$O$_3$, Ti$_2$O$_3$, and Al$_2$TiO$_5$ phases; according to the reported Al$_2$O$_3$–TiO$_2$ and Al$_2$O$_3$–Ti$_2$O$_3$ phase diagrams,\(^5\) a liquid oxide phase could not exist at 1 600°C. Recently, Matsuura \textit{et al.}\(^3\) and Kim \textit{et al.}\(^4\) also calculated the inclusion phase at 1 600°C. Nevertheless, the existence of a liquid oxide inclusion phase in the Fe–Al–Ti–O inclusion diagram has remained an open question, mainly due to lack of phase equilibrium data for the Al–Ti–O (Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$) system, especially at low oxygen partial pressures.

The phase diagram of the Al–Ti–O system has been partially investigated. Since Ti has more than one stable valence state, the phase equilibria are dependent on oxygen partial pressure. Although the phase diagram under oxidizing conditions is relatively well known,\(^5\) the diagram under reducing conditions has not been well investigated.

In the present study, thermodynamic modeling of the Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ system is performed based on all the available limited experimental data, and the resultant model is used to calculate phase equilibria for the Al$_2$O$_3$–TiO$_2$–TiO$_2$ system at various oxygen partial pressures. A revised inclusion diagram for Ti-bearing and Al-killed steels is proposed.

All thermodynamic calculations in the present study were performed using the FactSage thermochemical software.\(^6\)

2. Thermodynamic Modeling of the Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ System

The following phases have been observed in the Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ system:

- Slag (molten oxide phase): AlO$_{1.5}$–TiO$_{1.5}$–TiO$_2$.
- Corundum: Al$_2$O$_3$–rich solid solution with limited solubility of Ti$_2$O$_3$.
- Ilmenite: Ti$_2$O$_3$–rich solid solution with limited solubility of Al$_2$O$_3$.
- Rutile: TiO$_2$–rich solid solution with limited solubility of Ti$_2$O$_3$.

Stoichiometric compounds: Several Magnéli phases (Ti$_n$O$_{2n-1}$, \(n=4\)), Al$_2$TiO$_5$ (tialite), Al$_4$TiO$_8$ and Ti$_3$O$_5$ (pseudobrookite).

A. Molten Oxide (Slag)

The Modified Quasichemical Model\(^7\)–\(^10\) which takes into account short-range ordering of second-nearest-neighbor cations in the ionic melt, is used for modeling the slag. (The components of the slag are taken as AlO$_{1.5}$–TiO$_{1.5}$–TiO$_2$.)
and Ti$^{3+}$ ions are distributed as independent particles in the liquid solution, not as ion pairs.) The following short-range ordering quasichemical reactions are taken into account:

\[(A\text{-}A)+(B\text{-}B)=2(A\text{-}B), \quad \Delta G_{AB} \quad \ldots (1)\]

where \(A\) and \(B\) are Al$^{3+}$, Ti$^{3+}$ or Ti$^{4+}$, and \((A\text{-}B)\) represents a second-nearest-neighbor \(A\text{-}B\) pair. The Gibbs energies of this reaction \(\Delta G_{AB}\) are the model parameters, which can be expanded as empirical functions of composition. The Gibbs energies and all second-nearest-neighbor “coordination numbers” of the three liquid components used in the model are the same as in previous studies.\(^{11,12}\) That is, the coordination number of Ti$^{3+}$ is identical to that of Al$^{3+}$, which is 3/4 that of Ti$^{4+}$. Optimized model parameters for the Ti$_2$O$_3$–TiO$_2$ binary liquid phase were recently reported,\(^{12}\) while optimized parameters for the Al$_2$O$_3$–TiO$_2$ and Al$_2$O$_3$–Ti$_2$O$_3$ binary liquids are reported in the present study. The properties of the ternary slag solution are estimated from the optimized binary model parameters using an asymmetric “Tooop-like”\(^{13}\) approximation, with TiO$_2$ as the “asymmetric component”. No additional adjustable ternary model parameters are used for the liquid phase. The optimized model parameters are listed in Table 1.

**Table 1.** Optimized thermodynamic model parameters in the Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ system (J/mol, J/mol-K).

| Liquid phase |
|--------------|
| Ti$_2$O$_3$–TiO$_2$ binary | \(|G^0_{\text{corundum}}|=\frac{X_B G^0_A + X_A G^0_B + C_A}{x_B^2} + 2RT \ln \frac{x_A}{x_B} + C_B \quad \ldots (2)\)|
| Al$_2$O$_3$–TiO$_2$ binary | \(|G^0_{\text{ilmenite}}|=\frac{X_A G^0_B + C_A}{x_A^2} + 2RT \ln \frac{x_A}{x_B} + C_B \quad \ldots (3)\)|
| Al$_2$O$_3$–Ti$_2$O$_3$ binary | \(|G^0_{\text{Ilmenite}}|=\frac{X_A G^0_B + C_A}{x_B^2} + 2RT \ln \frac{x_A}{x_B} + C_B \quad \ldots (3)\) |

where \(A\) and \(B\) are Al$_2$O$_3$ and Ti$_2$O$_3$, \(G^0_A\) and \(G^0_B\) are the Gibbs energies of pure Al$_2$O$_3$ (corundum) and Ti$_2$O$_3$ (ilmenite) which are taken from the previous studies,\(^{11,12}\) \(X_A\) and \(X_B\) are the component mole fractions, and \(C_A\) and \(C_B\) are model parameters. \(C_A\) can be considered as the Gibbs

**B. Corundum (Al$_2$O$_3$) and Ilmenite (Ti$_2$O$_3$)**

The corundum phase is an Al$_2$O$_3$-rich solid solution, with a trigonal structure based on the hcp oxygen-packing scheme which dissolves a small amount of TiO$_2$. The ilmenite phase is a Ti$_2$O$_3$-rich solid solution, with a hexagonal structure, which dissolves a limited amount of Al$_2$O$_3$. In the absence of any experimental data, it is assumed that TiO$_2$ is stable only to a negligible extent in both phases. The molar Gibbs energies of the corundum and ilmenite phases are modeled as ideal ionic substitutional Henrian solutions by the following expressions:

\[G^0_{\text{corundum}}=(X_B G^0_A + X_A G^0_B + C_A) \quad \ldots (2)\]

\[G^0_{\text{ilmenite}}=(X_A G^0_B + C_A) + 2RT \ln \frac{x_A}{x_B} + C_B \quad \ldots (3)\]

No ternary model parameters were used. Notation as in reference [10].

**Ilmenite solid solution (Ti$_2$O$_3$ rich solid solution)**

\[G^0_{\text{TiO}_2, \text{ilmenite}} \quad \text{(hypothetical Al$_2$O$_3$ with ilmenite structure) = } \quad G^0_{\text{Al$_2$O}_3, \text{corundum}} + 50208.0\]

**Corundum solid solution (Al$_2$O$_3$ rich solid solution)**

\[G^0_{\text{Al$_2$O}_3, \text{corundum}} \quad \text{(hypothetical TiO$_2$ with corundum structure) = } \quad G^0_{\text{TiO}_2, \text{ilmenite}} + 108784.0\]

**Stoichiometric line compounds**

(standard enthalpies of formation from the elements, absolute entropy, and heat capacity)

\[\Delta H^o_{\text{Al$_2$TiO}_3}= -2577174.0 \quad S^o_{\text{Al$_2$TiO}_3} = 128.448\]

\[C_p = 249.290 - 4.806\times10^6 T^{-2} - 1350.107 T^{-2} + 5.160\times10^6 T^{-3}\]

\[\Delta H^o_{\text{Al$_2$TiO}_3}= -4194883.4 \quad S^o_{\text{Al$_2$TiO}_3} = 211.576\]

\[C_p = 395.840 - 1.1634\times10^6 T^{-2} - 1925.37 T^{-2} + 1.505\times10^6 T^{-3}\]

Magnéli phases (Ti$_{2n}$O$_{3n+1}$, \(n \geq 4\)) and Ti$_2$O$_3$: taken from Kang et al.\(^{12}\)

The Gibbs energies of all pure solid and liquid phases were taken from references \([6, 11, 12]\).

Thermodynamic parameters for the rutile solid solution are taken from Kang et al.\(^{12}\)

\[G^o = \Delta H^o_{\text{Al$_2$TiO}_3} + \int \frac{C_p}{264.15} + \int \frac{(C_p/T)T}{264.15} \]
energy of transition of pure Al$_2$O$_3$ with the corundum structure to hypothetical pure Al$_2$O$_3$ with the ilmenite structure, while $C_p$ can be interpreted analogously. The factor “2” appears in Eqs. (2) and (3) because each mole of Al$_2$O$_3$ or Ti$_2$O$_3$ supplies two moles of cations which mix substitutionally on the cationic sublattice. The optimized parameters are given in Table 1.

C. Rutile (TiO$_2$)

Rutile dissolves a small amount of Ti$_2$O$_3$ and is often written as TiO$_{2-δ}$. The defect structure of rutile has not been confirmed. Eriksson and Pelton$^{11}$ modeled the rutile solid solution using a simple ionic substitutional Henrian solution model. The model parameters were reoptimized by Kang et al.$^{12}$ in order to reproduce the experimental solubility data over a wide range of temperatures. The thermodynamic model of Kang et al.$^{12}$ is adopted in the present study with no modification.

D. Stoichiometric Compounds

The Gibbs energy functions of several Magnéli phases (Ti$_{2n}$O$_{4n-1}$, $n$=4) and Ti$_2$O$_3$ are taken from the previous studies$^{11,12}$ with no modification. The Gibbs energies of Al$_2$TiO$_5$ (tialite) and Al$_4$TiO$_8$ are evaluated in the present study. In the absence of any experimental evidence to the contrary, all of these phases are assumed to be stoichiometric compounds.

3. Critical Evaluation and Optimization of the Al$_2$O$_3$–Ti$_2$O$_3$–TiO$_2$ System

3.1. Ti$_2$O$_3$–TiO$_2$ Binary System

Figure 1 shows the calculated phase diagram of the Ti–O (Ti$_2$O$_3$–TiO$_2$) system. This system was critically evaluated and optimized by Eriksson and Pelton.$^{11}$ Recently, Kang et al.$^{12}$ reoptimized the model parameters of the liquid oxide and rutile phases in order to reproduce the phase diagram more accurately. The details of the thermodynamic modeling and model parameters can be found in the previous study.$^{12}$ Iso-oxygen partial pressure lines in the liquid phase are also calculated and plotted in Fig. 1. As can be seen, the equilibrium amounts of Ti$_2$O$_3$ and TiO$_2$ in the liquid phase vary significantly with oxygen partial pressure and temperature.

3.2. Al$_2$O$_3$–TiO$_2$ Binary System

Figure 2 shows the calculated optimized phase diagram of the Al$_2$O$_3$–TiO$_2$ system in air. The diagram was first studied by von Wartenberg and Reusch$^{15}$ and by Bunting.$^{15}$ The former gave the intermediate compound as Al$_2$Ti$_2$O$_7$, while the latter reported Al$_2$TiO$_5$ (tialite). The phase relationships reported by Land et al.$^{16}$ from visual techniques combined with petrographic and X-ray studies suggest that tialite melts congruently at 1863°C, but due to the extreme experimental conditions of high temperature and high melt viscosity, the possibility of incongruent melting could not be ruled out. They also reported a transformation temperature of tialite at 1823°C; this finding is in doubt according to the later study by Azimov et al.$^{17}$ The solid solubility of TiO$_2$ in Al$_2$O$_3$ was reported$^{18}$ as 0.6 mol%, while no solubility of Al$_2$O$_3$ in TiO$_2$ was detected. In the present evaluation, no solid solubilities were considered in either terminal solid solution. Goldberg,$^{19}$ in a more recent study, reported a congruent melting point of tialite at 1850°C and a eutectic at 1703°C and 80 mol% TiO$_2$ from quenching and optical microscopic analysis. Lejus et al.$^{19}$ found two new compounds with compositions between 33 and 40 mol% TiO$_2$ which are stable in the approximate temperature range between 1800°C and 1900°C. In the present study these two compounds were both approximated by the single compound Al$_2$TiO$_5$. Kato et al.$^{20}$ found that Al$_2$TiO$_5$ decomposes to Al$_2$O$_3$ and TiO$_2$ below 1280°C. Woermann$^{21}$ performed a similar study and reported the decomposition temperature as 1264°C. In the present evaluation the more recent value by Woermann is adopted.

The low temperature heat capacity of Al$_2$TiO$_5$ from 52 to 298 K was measured by King$^{22}$ and the entropy at 298.15 K was calculated as 109.6 ± 0.8 J/mol-K. Bonnickson$^{23}$ measured the high temperature heat content of Al$_2$TiO$_5$ from 411 to 1803 K. Due to the dissociation of Al$_2$TiO$_5$ at around 1200–1300°C, both King and Bonnickson took special care in the preparation of samples. These experimental data were re-evaluated and compiled by Robie et al.$^{24}$ and Berman and Brown.$^{25,26}$ No experiments to determine the standard enthalpy of formation, $\Delta H_{f}^{\circ}$, of Al$_2$TiO$_5$ have been performed. Kubaschewski$^{27}$ provided a rough estimation of the enthalpy of formation of Al$_2$TiO$_5$ from its oxides (Al$_2$O$_3$ and TiO$_2$) at 298 K as $-8.4 \pm 8.4$ kJ/mol but gave no detailed explanation. These results were also tabulated later.
by Kubaschewski and Alcock.\(^\text{28}\) Combining this estimated enthalpy of formation with the entropy reported by King\(^\text{22}\) yields a negative Gibbs energy of formation of Al\(_2\)TiO\(_5\) from the pure oxides at 298 K of −10.7 J/mol, which is inconsistent with the reported\(^\text{20,23}\) decomposition of Al\(_2\)TiO\(_5\) below about 1 250°C.

In the present study, \(C_p\) of Al\(_2\)TiO\(_5\) is taken with no modification from the compilation of Berman and Brown\(^\text{25,26}\) which is based on the experimental data of Bonnickson.\(^\text{23}\) \(\Delta H_{298}^\circ\) and \(S_{298}\) were then chosen in order to reproduce the phase diagram. The optimized value of \(S_{298}\) differs from that reported by King\(^\text{22}\) by 18.8 J/mol-K, which is well outside the stated uncertainty. It was not possible to reproduce the reported entropy in the optimization simultaneously with all the other data, in particular with the melting and decomposition temperatures of Al\(_2\)TiO\(_5\), while still retaining reasonable thermodynamic properties for the liquid phase. The value of King is most likely that of the low-temperature metastable ordered phase, while the present optimized value applies to the high-temperature disordered phase.

For Al\(_2\)TiO\(_5\), \(C_p\) was predicted by the method of Berman and Brown\(^\text{25,26}\) while \(\Delta H_{298}^\circ\) and \(S_{298}\) were obtained from the phase diagram analysis in order to give a stability range between 1 800 and 1 900°C. In order to reproduce the reported liquidus and eutectic temperatures, small positive model parameters for the binary Al\(_2\)O\(_3\)–Ti\(_2\)O\(_3\) liquid phase were required as shown in Table 1.

### 3.3. Al\(_2\)O\(_3\)–Ti\(_2\)O\(_3\) Binary System

The calculated optimized phase diagram is shown in Fig. 3 along with experimental points. McKee and Aleshin\(^\text{29}\) reported sub-liquidus phase equilibria for this system. Mixtures of Ti\(_2\)O\(_3\) and Al\(_2\)O\(_3\) were heated in H\(_2\) gas atmospheres. After quenching, the solubility of Ti\(_2\)O\(_3\) in the Al\(_2\)O\(_3\) corundum solution was determined from the variation of the lattice parameters measured by an X-ray diffraction technique. No intermediate solid phases were found between the Ti\(_2\)O\(_3\) and Al\(_2\)O\(_3\) terminal solid solutions. Later, Belon and Forester\(^\text{30}\) investigated the phase diagram using both an X-ray diffraction technique and high temperature microscopic measurements. Ti\(_2\)O\(_3\) was prepared by the reduction of TiO\(_2\) in a vacuum chamber at 1 850°C. The mixtures of this Ti\(_2\)O\(_3\) and Al\(_2\)O\(_3\) were used for all subsequent experiments under vacuum. From lattice parameter measurements, they reported a maximum solubility of Ti\(_2\)O\(_3\) in Al\(_2\)O\(_3\) of 12.5 mol% near 1 700°C. The solidus and eutectic temperatures were determined from high temperature microscopic measurements using an optical pyrometer. The lowest melting temperature of the solid mixture of Ti\(_2\)O\(_3\) and Al\(_2\)O\(_3\) was found to be about 1 695°C. Horibe and Kuwabara\(^\text{31}\) performed similar experiments to determine the solubility of Ti\(_2\)O\(_3\) in solid Al\(_2\)O\(_3\) in equilibrium with either the liquid or ilmenite. They prepared the Ti\(_2\)O\(_3\) by reducing TiO\(_2\) under CO gas at 1 400°C. This preparation was confirmed by subsequent X-ray diffraction measurements and determination of its melting temperature to be approximately 1 800°C. All subsequent experiments were carried out under high purity Ar gas atmospheres. They reported that the lowest melting temperature of the system is about 1 720°C and that the solubility of Ti\(_2\)O\(_3\) in Al\(_2\)O\(_3\) is 2.7 mol% at 1 710°C.

Recently, Ohta and Morita\(^\text{32}\) determined the solubility of Ti\(_2\)O\(_3\) in solid Al\(_2\)O\(_3\) from lattice parameter changes after equilibrating mixtures of TiO\(_2\) and Al\(_2\)O\(_3\) under gaseous atmospheres with \(P_{O_2} = 10^{-16}\) bar at 1 600°C. They also studied the solubility of Al\(_2\)O\(_3\) in the Ti\(_2\)O\(_3\) ilmenite solid solution using the same technique. Mizoguchi and Ueshima\(^\text{33}\) performed ternary phase equilibriations in the CaO–Ti\(_2\)O\(_3–\)Al\(_2\)O\(_3\) system at \(P_{O_2} = 10^{-14}–10^{-15}\) bar at 1 600°C. Several three-phase samples: ‘liquid + Ti\(_2\)O\(_3\) solution + Al\(_2\)O\(_3\) solution’ were found. After quenching, the composition of each phase was analyzed by SEM-EDS. The size of each phase was large enough to permit reasonably accurate EDS analysis. The solubility of CaO in both Ti\(_2\)O\(_3\) and Al\(_2\)O\(_3\) solid solutions were detected to be zero. Mizoguchi and Ueshima\(^\text{33}\) reported 21.3 mol% Al\(_2\)O\(_3\) solubility in the Ti\(_2\)O\(_3\) solid solution at 1 600°C. This more direct phase analysis using EDS\(^\text{13}\) of the solubility limits of the Al\(_2\)O\(_3\) and Ti\(_2\)O\(_3\) solid solutions was given the highest weight in the present evaluation.

Figure 3 shows the calculated optimized phase diagram of the Al\(_2\)O\(_3–\)Ti\(_2\)O\(_3\) system under reducing conditions (calculated at \(P_{O_2} = 10^{-15}\) bar). Metallic phases are not considered in the calculation.

The quasichemical model parameters for the liquid AlO\(_1.5–\)TiO\(_2\) solutions were assumed to be the same as the parameters for the liquid in the AlO\(_1.5–\)TiO\(_2\) system. With this assumption, the liquidus data are reproduced within experimental error limits. Although the model parameters for the liquid AlO\(_1.5–\)TiO\(_2\) phase might be slightly adjusted to reproduce the experimental data even more closely, this was judged not to be justified by the experimental accuracy.

### 3.4. Al\(_2\)O\(_3–\)Ti\(_2\)O\(_3–\)TiO\(_2\) Ternary System

Figure 4 shows the predicted liquidus projection of the Al\(_2\)O\(_3–\)Ti\(_2\)O\(_3–\)TiO\(_2\) system. No ternary parameters are used in the Al\(_2\)O\(_3–\)Ti\(_2\)O\(_3–\)TiO\(_2\) liquid oxide phase in the present study. No phase diagram measurement is available for this ternary system. As mentioned before, the Gibbs energy of the ternary liquid oxide was calculated from the binary pa-
Porous Ti oxide phases appear at different temperatures. When (when the Al content, \([\text{Al}]\), is about 500 wt ppm).

Equilibrium liquid \(\text{Fe}\) on Fig. 6. The oxygen partial pressure for the two-phase 1 500°C. Iso-oxygen partial pressure lines are also plotted at 1 600°C and even over a small composition region at can exist over a considerable region of the ternary diagram model predicted phase diagrams for the \(\text{Al}_2\text{O}_3–\text{Ti}_2\text{O}_3–\text{TiO}_2\) system at 1 600°C, of great importance. When \(\text{Ti}_2\text{O}_3\) and \(\text{TiO}_2\) in the liquid phase as well as the sub-solidus equilibria can be changed significantly. Predicted phase diagrams for the \(\text{Al}_2\text{O}_3–\text{Ti}_2\text{O}_3–\text{TiO}_2\) system at different oxygen partial pressures are presented in Fig. 5. As can be seen in the figure, the phase diagrams at \(P_{\text{O}_2}\) \(>10^{-5}\) bar are similar to the phase diagram in air. With decreasing oxygen partial pressure, liquidus temperatures decrease and the solubility of \(\text{Ti}_2\text{O}_3\) in the \(\text{Al}_2\text{O}_3\) corundum phase becomes more noticeable. When \(P_{\text{O}_2}<10^{-8}\) bar, various Ti oxide phases appear at different temperatures. When \(P_{\text{O}_2}<10^{-14}\) bar, the \(\text{Ti}_2\text{O}_3\) ilmenite solid solution becomes stable as a primary solid phase and the liquidus temperature increases. When \(P_{\text{O}_2}=10^{-15}\) bar, oxides can be reduced to a metallic phase above 1 900°C.

**Fig. 4.** Calculated (predicted) liquidus projection of the \(\text{Al}_2\text{O}_3–\text{Ti}_2\text{O}_3–\text{TiO}_2\) system. Temperatures in °C.

Parameters using an asymmetric “Toop-like” approximation\(^\text{13}\) with \(\text{TiO}_2\) as the asymmetric component. No ternary solid phases have been reported. According to the present thermodynamic prediction, the minimum ternary eutectic temperature is calculated to be 1 496°C at the (molar) composition \(0.23\text{Al}_2\text{O}_3–0.23\text{Ti}_2\text{O}_3–0.54\text{TiO}_2\).

Depending on the oxygen partial pressure, the relative amounts of \(\text{Ti}_2\text{O}_3\) and \(\text{TiO}_2\) in the liquid phase as well as the sub-solidus equilibria can be changed significantly. The experimental results for the \(\text{Al}_2\text{O}_3–\text{Ti}_2\text{O}_3–\text{TiO}_2\) system are less than 1 mol% under steelmaking conditions. How- ever, the solubility of \(\text{Al}_2\text{O}_3\) in the ilmenite solid solution can be as high as 16 mol% in equilibrium with the \(\text{Al}_2\text{O}_3\). Partial pressures. Ruby-Meyer et al.\(^\text{1}\) reported liquid \(\text{Al}_2\text{O}_3–\text{TiO}_2\) (more correctly, \(\text{Al}_2\text{O}_3–\text{Ti}_2\text{O}_3–\text{TiO}_2\)) inclusions in molten steel containing 0.1% Mn–0.03% Si–Al–Ti at 1 580°C. (Thermodynamic calculations using FactSage\(^\text{6}\) show that neither Mn nor Si form oxide inclusions under their experimental conditions). Park et al.\(^\text{34}\) also observed Al–Ti–O inclusions during reoxidation experiments on Al-killed and Ti-bearing steel at 1 600°C. In their study, two-layered inclusions of an unknown Al–Ti–O phase covering a core \(\text{Al}_2\text{O}_3\) solid were frequently observed. The EPMA analysis for the Al–Ti–O phase showed molar ratios Ti/Al of the phase of between 1.0 and 1.5. In addition, the surface shape of the phases was not faceted but spherical, which is typical of a liquid phase. Very recently, Doo et al.\(^\text{35}\) also reported similar two-layered inclusions in Al-killed and Ti-bearing steel sampled in the RH process at 1 600°C. The analyzed value of the molar ratio Ti/Al for the spherical Al–Ti–O phase was about 1.6. These experimental results support the contention that a liquid Al–Ti–O phase exists at 1 600°C with a molar ratio Ti/Al=1.0–1.6 when in equilibrium with \(\text{Al}_2\text{O}_3\). This composition is close to the predicted liquid composition at \(\text{Al}_2\text{O}_3\) saturation at 1 600°C in Fig. 6.

**4. Application to Al–Ti Deoxidation in Secondary Steelmaking Process**

As mentioned earlier, there are discrepancies in the Fe–Al–Ti–O inclusion diagram due to the lack of phase equilibrium data for the Al–Ti–O system. Based on the present optimization results of the Al–Ti–O oxide system, the inclusion diagram was recalculated. In order to construct the Fe–Al–Ti–O inclusion diagram, both oxide and liquid steel databases containing all the elements are necessary.

For the oxide database, the present model parameters for the Al–Ti–O system were combined with the previously optimized parameters for the Fe–Ti–O (FeO–Fe\(_2\)O\(_3\)–\(\text{TiO}_2\)) and Fe–Al–O (FeO–Fe\(_2\)O\(_3\)–\(\text{Al}_2\text{O}_3\)) systems. The integrated thermodynamic database includes a liquid oxide phase \(\text{AlO}_{1.5–1.7}\text{TiO}_{1.5–1.7}\text{FeO}_{0.5–0.7}\text{TiO}_{1.5–1.7}\) and solid solution phases of corundum, rutile, ilmenite, pseudobrookite, etc. with possible dissolution of FeO and Fe\(_2\)O\(_3\). For the molten steel phase, our recently developed liquid steel database which employs the associate model\(^\text{30}\) was used. In the associate model, the interactions of strong deoxidants M (such as M=Al, Ti, Ca, Mg, …) with dissolved oxygen are modeled by explicitly considering the formation of \(\text{M}_3\text{O}\) associates or “molecules” in solution. This model has been shown to have very good predictive capability over wide ranges of temperature and composition.

**Fig. 7** shows a revised inclusion diagram for \(\text{Al}+\text{Ti}\) complex deoxidation at 1 600°C. The corresponding composition trajectories with iso-[\(\text{Ti}\)] content are calculated in **Fig. 8**. In comparison with our previous diagram,\(^\text{21}\) the most noticeable differences are the existence of a liquid oxide phase field and the disappearance of the solid \(\text{Al}_2\text{TiO}_3\) field. According to the calculations, the solubilities of \(\text{Al}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3\), \(\text{Ti}_2\text{O}_3\) in the corundum and rutile solid solutions are less than 1 mol% under steelmaking conditions. However, the solubility of \(\text{Al}_2\text{O}_3\) in the ilmenite solid solution is limited to a maximum of 16 mol% in equilibrium with the \(\text{Al}_2\text{O}_3\).
Fig. 5. Calculated (predicted) phase diagrams of the Al₂O₃–Ti₂O₃–TiO₂ system at various oxygen partial pressures. (a) In air, (b) $P_{O_2} = 10^{-3}$, (c) $P_{O_2} = 10^{-4}$, (d) $P_{O_2} = 10^{-5}$, (e) $P_{O_2} = 10^{-6}$, (f) $P_{O_2} = 10^{-10}$, (g) $P_{O_2} = 10^{-15}$ bar.
corundum phase. The somewhat unusual shape of the ilmenite stability region is due to this solubility of Al₂O₃. Although the liquid inclusion region appears narrow in the diagram, the composition of the liquid inclusion phase varies rather widely between Al₂O₃ and Ti₃O₅ saturation as can be seen in Fig. 8. At very low concentrations of Al and Ti ([Al]<10 ppm and [Ti]<20 ppm), the oxygen partial pressure can be high enough to cause FeO to dissolve in the liquid oxide phase to about 10 wt%. This is the reason that the liquid region becomes wider at low Al–Ti contents in Fig. 7 and that the Magnéli phases and Al₂TiO₅ phase disappear in Fig. 8. However, when [Al]>10 ppm, the FeO content in the liquid oxide phase becomes less than 1 wt%, and the liquid phase is virtually a ternary Al₂O₃–Ti₂O₃–TiO₂ phase. Although the equilibrium soluble oxygen concentration passes through minima at log[wt% Al]=−1.2 and at log[wt% Ti]=−0.5 and then increases again with increasing [Al] and [Ti], the activity of oxygen continues to decrease as [Al] and [Ti] increase. The liquid inclusion phase disappears when log[wt% Ti]<−0.3 and log[wt% Al]>−1.5. In this concentration range of the liquid steel, the oxygen partial pressure is lower than 10⁻¹⁵ bar. As can be seen in Fig. 6, no liquid oxide phase can exist in this oxygen partial pressure range.

Many researchers³⁹–⁴² have reported that nozzle clogging is more severe in the case of Ti-bearing Al-killed steel than Ti-free steel. Al–Ti–O inclusions are frequently observed in clogged nozzles for Ti-bearing Al-killed steels.⁴⁰–⁴² However, the nature of this Al–Ti–O phase which causes nozzle clogging has not been well investigated. Recently, Basu et al.⁴² investigated various aspects of secondary steelmaking causing nozzle clogging for Ti-bearing Al-killed steels. According to their study, the significant difference between nozzle clogging of Ti-bearing steel and Ti-free steel is the existence of Al–Ti–O inclusions covering solid Al₂O₃. They reported that the nozzle clogging for Ti-bearing Al-killed steel is strongly related to the reoxidation of molten steel in the tundish. Park et al.³⁴ reported that a two-layered inclusion of the Al–Ti–O phase with core Al₂O₃, which is identical to the inclusion causing the nozzle clogging,⁴² was frequently generated by the reoxidation of Ti-bearing and Al-killed molten steel by high-SiO₂ tundish slags. Thus, according to the present study, this Al–Ti–O phase which causes the nozzle clogging is most probably a liquid oxide phase saturated with core solid Al₂O₃ oxide.

In order to understand nozzle clogging as well as the inclusions in Ti-bearing and Al-killed steel more completely, it will be necessary to investigate thermodynamic properties such as the phase diagram of the Al–Ti–O system (Al₂O₃–Ti₂O₃–TiO₂) under various oxygen partial pressures as well as the wetting behavior of the liquid Al₂O₃–Ti₂O₃–TiO₂ phase with refractories and molten steel.

5. Summary

A critical evaluation and optimization of all available phase diagram and thermodynamic data for the Al₂O₃–Ti₂O₃–TiO₂ system has been made, and a database of model parameters has been prepared. Based on the thermodynamic modeling, the ternary phase equilibria of the Al₂O₃–Ti₂O₃–TiO₂ system under various oxygen partial pressures have been predicted for the first time. The phase
diagram of the Al\textsubscript{2}O\textsubscript{3}–Ti\textsubscript{2}O\textsubscript{3}–TiO\textsubscript{2} system indicates the possible existence of a liquid phase at 1600°C under steelmaking conditions. Together with the model and database for molten steel and the FactSage software for Gibbs energy minimization, thermodynamic calculations have been performed to calculate the inclusion diagram for Al–Ti deoxidation at 1600°C. The calculations show that a liquid Al\textsubscript{2}O\textsubscript{3}–Ti\textsubscript{2}O\textsubscript{3}–TiO\textsubscript{2} inclusion phase can exist in Al-killed and Ti-bearing steel at 1600°C. This appears to be strongly related to the nozzle clogging phenomenon.

REFERENCES
1) F. Ruby-Meyer, J. Lehmann and H. Gaye: Scand. J. Metall., 29 (2000), 206.
2) I.-H. Jung, S. Decterov and A. D. Pelton: ISIJ Int., 44 (2004), 527.
3) H. Matsuura, C. Wang, G. Wen and S. Sridhar: ISIJ Int., 47 (2007), 1265.
4) W.-Y. Kim, J.-O. Jo, C.-O. Lee, D.-S. Kim and J.-J. Pak: ISIJ Int., 48 (2008), 17.
5) Slag Atlas, 2nd ed., ed. by Verein Deutscher Eisenhüttenleute, Verlag Stahleisen GmbH, Düsseldorf, (1995), 48.
6) C. W. Bale, P. Charrand, S. A. Degterov, G. Eriksson, K. Hack, R. B. Mahfoud, I. Melançon, A. D. Pelton and S. Petersen: Calphad, 26 (2002), 189.
7) A. D. Pelton and M. Blander: Proc. 2nd Int'l Symposium on Metallurgical Slags and Fluxes, TMS-AIME, Warrendale, PA, (1984), 281.
8) A. D. Pelton and M. Blander: Metall. Trans. B, 17B (1986), 805.
9) A. D. Pelton, S. A. Decterov, G. Eriksson, C. Robelin and Y. Dessureault: Metall. Mater. Trans. B, 31B (2000) 651.
10) A. D. Pelton and P. Charrand: Metall. Mater. Trans. A, 32A (2001), 1355.
11) G. Eriksson and A. D. Pelton: Metall. Trans. B, 24B (1993), 795.
12) Y. B. Kang, I.-H. Jung and H.-G. Lee: Calphad, 30 (2006), 235.
13) A. D. Pelton: Calphad, 25 (2001), 319.
14) H. von Wartenberg and H. J. Reusch: Z. Anorg. Allg. Chem., 207 (1932), 1.
15) E. N. Bunting: Bur. Standards J. Research, 11 (1933), 719.
16) S. M. Lang, C. J. Fillmore and L. H. Maxwell: J. Res. Natl. Bur. Stand., 48 (1952), 298.
17) S. A. Azimov, D. G. Gulamova, N. N. Mel’nik, M. Kh. Sarkisova, S. Kh. Suleimanov and L. M. Tsapenko: Izv. Akad. Nauk SSSR, Neorg. Mater., 20 (1984), 469.
18) D. Goldberg: Rev. Int. Hautes Temp. Refract., 5 (1968), 181.
19) A. M. Lejus, D. Goldberg and A. Revcolevschi: C. R. Acad. Sci. Paris, Ser. C, 263 (1966), 1223.
20) E. Kato, K. Daimon and J. Takahashi: J. Am. Ceram. Soc., 63 (1980), 355.
21) E. Woermann: Private communication, (1990).
22) E. G. King: J. Am. Chem. Soc., 77 (1955), 2150.
23) K. R. Bonnickson: J. Am. Ceram. Soc., 77 (1955), 2152.
24) R. A. Robie, B. S. Hemingway and J. R. Fisher: Thermodynamic Properties of Minerals and Related Substances at 298.15 K and 1 bar Pressure and at Higher Temperatures, U.S. Government Printing Office, Washington D.C., (1978), 456.
25) R. G. Berman and T. H. Brown: Contrib. Mineral. Petrol., 89 (1985), 168.
26) R. G. Berman and T. H. Brown: Contrib. Mineral. Petrol., 94 (1986), 262.
27) O. Kubaschewski: High Temp.-High Press., 4 (1972), 1.
28) O. Kubaschewski and C. B. Alcock: Metallurgical Thermochemistry, Pergamon, London, (1979), 268.
29) W. D. McKee, Jr. and E. Aleshin: J. Am. Ceram. Soc., 46 (1963), 54.
30) L. Belon and H. Forestier: Compt. Rend., 258 (1964), 4282.
31) T. Horibe and S. Kawahara: Kagaku Zasshi, 67 (1964) 276.
32) M. Ohta and K. Morita: ISIJ Int., 42 (2002), 474.
33) T. Mizoguchi and Y. Ueshima: Tetsu-to-Hagané, 91 (2005), 376.
34) K.-H. Park, I.-H. Jung, P. C. H. Rhee and H.-G. Lee: ISIJ Int., 44 (2004), 1669.
35) W.-C. Doo, D.-Y. Kim, S.-C. Kang and K.-W. Yi: Met. Mater.-Int., 13 (2007), 249.
36) G. Eriksson, A. D. Pelton, E. Woermann and A. Ender: Ber. Bunsenges. Phys. Chem., 100 (1996), 1839.
37) S. A. Decterov, I.-H. Jung, E. Jak, Y.-B. Kang, P. Hayes and A. D. Pelton: Proc. VII Int'l. Conf. on Molten Slags, Fluxes and Salts, South African Inst. Mining & Metallurgy, Johannesburg, (2004), 839.
38) I.-H. Jung, S. Decterov and A. D. Pelton: Metall. Mater. Trans. B, 35B (2004), 493.
39) W.-K. Jung: POSCO Internal Research Report, (1996).
40) Y. Hiraga, Y. Yashima and K. Fuji: Taikabutsu Overseas, 15 (1995), 22.
41) S. Ogibayashi: Taikabutsu Overseas, 15 (1995), 3.
42) S. Basu, S. K. Choudhary and N. U. Girase: ISIJ Int., 44 (2004), 1653.