Critical Thermodynamic Evaluation and Optimization of the CaO–MnO–SiO$_2$ and CaO–MnO–Al$_2$O$_3$ Systems

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(Received on November 10, 2003; accepted in final form on March 3, 2004)

A complete review, critical evaluation, and thermodynamic optimization of phase equilibrium and thermodynamic properties of the CaO–MnO–SiO$_2$ and CaO–MnO–Al$_2$O$_3$ systems at 1 bar pressure are presented. The molten oxide phase was described by the Modified Quasichemical Model, the Gibbs energy of the divine solid solution was modeled with the Compound Energy Formalism, and the wollastonite s.s., rhodonite s.s., and Ca$_2$Si$_2$O$_7$ solutions were modeled by polynomial expansions of the excess Gibbs energy. Sets of optimized model parameters for all phases were obtained which reproduce all available reliable thermodynamic and phase equilibrium data within experimental error limits from 25°C to above the liquidus temperatures over the entire ranges of composition. The liquidus surface of the CaO–MnO–Al$_2$O$_3$ system, which has not been measured, has been predicted. Complex phase relationships in these systems have been elucidated, and discrepancies among the data have been resolved. Phase equilibria between liquid slag and manganese alloys have been calculated. The database of model parameters can be used along with software for Gibbs energy minimization in order to calculate any phase diagram section or thermodynamic property.

KEY WORDS: solution thermodynamics; CaO–MnO–SiO$_2$ system; CaO–MnO–Al$_2$O$_3$ system; manganese alloy production; phase equilibria.

1. Introduction

The CaO–MnO–Al$_2$O$_3$–SiO$_2$ system is of interest for inclusion control in Mn/Si-killed steel. Mn/Si complex deoxidation is indispensable for the production of high-value steel such as tire-cord steel, valve-spring steel and high-Ni steel (Fe–36mass%Ni Invar steel) in order to avoid the harmful effects of solid Al$_2$O$_3$ inclusions which can be formed when Al is used as deoxidizer. Al$_2$O$_3$ inclusions usually cause wire breakage during tire-cord production, whereas inclusions should be deformable during the wire-making process. Usually, Mn/Si deoxidation results in MnO–SiO$_2$–Al$_2$O$_3$ inclusions of low melting temperature. However, the inclusions can be transformed to CaO–MnO–SiO$_2$–Al$_2$O$_3$ inclusions by reaction with top slag in the ladle. In order to control inclusions accurately, inclusion engineering, based on the thermodynamic relations between inclusions and liquid steel, should be carried out during the secondary refining stage in the ladle and tundish. The CaO–MnO–SiO$_2$–Al$_2$O$_3$ system is also a key system in the production of manganese alloys, and is of geological importance.

As part of a wider research project to extend the $P^A$C$^T$ oxide databases, the CaO–MnO–SiO$_2$–Al$_2$O$_3$ system has been completely evaluated and thermodynamically optimized. In the present article we present the optimization results for the CaO–MnO–SiO$_2$ and CaO–MnO–Al$_2$O$_3$ systems. In a subsequent article, the present results and previous optimizations for the CaO–Al$_2$O$_3$–SiO$_2$, CaO–MnO–Al$_2$O$_3$–SiO$_2$, and MnO–Al$_2$O$_3$–SiO$_2$ systems will be combined to complete the thermodynamic modeling of the CaO–MnO–SiO$_2$–Al$_2$O$_3$ system.

In a thermodynamic “optimization” of a system, all available thermodynamic and phase-equilibrium data are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner. A small set of model parameters is obtained. This is ideal for computer storage and calculation of properties and phase diagrams.

A number of previous studies report thermodynamic modeling of the CaO–MnO–SiO$_2$ and CaO–MnO–Al$_2$O$_3$ systems, however, these studies were limited to the liquid slag phase and none completely describe the entire system. The present article is a complete critical review of all thermodynamic and phase diagram data at 1 bar total pressure for the two ternary systems, including data on alloy/slag equilibria. The thermodynamically consistent phase diagrams, back-calculated from the model parameters, elucidate the complex phase relationships in these systems, and phase equilibria are predicted in composition and
temperature regions where measurements phase not been reported. In particular, the liquidus surface of the CaO–MnO–Al2O3 system, which has not yet been measured, is predicted. The phase equilibria calculated from the model parameters are the best available estimates of the true values since they are based on a consistent critical evaluation of all available types of data simultaneously.

All binary subsystem (CaO–MnO, 11) CaO–SiO2,12) CaO–Al2O3,13) MnO–SiO2,14) MnO–Al2O3,15) and MnO–Al2O3,3) have previously been critically evaluated and optimized by the authors, and these studies are used as the starting point in the present study.

All thermodynamic calculations have been performed with the FactSage thermodynamic computing system.16) Phase equilibria are calculated by global Gibbs energy minimization. By coupling the presently developed database with other evaluated F*A*C*T databases for metallic solutions, gases, etc., FactSage can be used to compute complex slag/metal/solid/gas equilibria. For example, phase equilibria between CaO–MnO–SiO2–Al2O3 inclusions and alloy phases can be simulated and studied.

2. Thermodynamic Models

Thermodynamic models for solution phases in the present systems are summarized below, and all optimized model parameters are listed in Table 1.

2.1. Molten Oxide (Slag)

For the molten oxide (slag) phase, the Modified Quasichemical Model17,18) was used. This model has been recently further developed and summarized.19,20) Short-range-ordering is taken into account by considering second-nearest-neighbor pair exchange reactions. For example, for the CaO–MnO–SiO2–Al2O3 slag, these reactions are:

\[(A-A) + (B-B) = 2(A-B) \Delta g_{AB} \] ........................(1)

where A and B are Ca, Mn, Al, and Si, and (A–B) represents a second-nearest-neighbor A–B pair. The parameters of the model are the Gibbs energies \( \Delta g_{AB} \) of these reactions, which may be expanded as empirical functions of composition. Although manganese can exist in the trivalent state in the slag at high oxygen partial pressures, in the present study only divalent manganese is considered to exist in the slag.

The binary model parameters obtained by optimization/evaluation of all the data in the binary subsystems, are given in Refs. 3, 4, 11, 12) along with the second-nearest-neighbor "coordination numbers" of Ca, Mn, Al and Si used in the Modified Quasichemical Model. The "asymmetric approximation"17,18) was used for the CaO–MnO–SiO2 system, with SiO2 as the "asymmetric component"; in order to estimate the Gibbs energy of the ternary liquid given from the binary parameters. In the case of the CaO–MnO–Al2O3 system, the asymmetric approximation17,18) was used with Al2O3 as the "asymmetric component". In order to reproduce the measured ternary phase diagram of the CaO–MnO–Al2O3 system, one small optimized ternary model parameter was added in the present study. No ternary parameters were used for the CaO–MnO–Al2O3 system. The optimized ternary model parameters are listed in Table 1.

| Table 1. Optimized model parameters of solutions in the CaO–MnO–SiO2 and CaO–MnO–Al2O3 systems (J/mol).1 |
|------------------|------------------|
| Gibbs energy of an "end-member", \( (A–A) \) | Gibbs energy of an "end-member", \( (B–B) \) |
| \( G(AA) \) | \( G(BB) \) |
| \( GCAO(\text{MnO}) \) | \( GCSiO2(\text{MnO}) \) |
| \( GCAO(\text{SiO2}) \) | \( GCSiO2(\text{SiO2}) \) |

2.2. Olivine Solid Solution

The olivine solid solution has two distinct octahedral sublattices, called \( M_1 \) and \( M_2 \):21)

\[(Ca^{2+}, Mn^{2+})_2\{\text{SiO}_4 \} \] ........................(2)

where cations shown within a set of brackets occupy the same sublattice.

Because \( M_2 \) sites are larger than \( M_1 \) sites, \( Ca^{2+} \) (which is larger than \( Mn^{2+} \)) prefers to enter the \( M_1 \) sites. For the olivine solution, the model is developed within the framework of the Compound Energy Formalism (CEF).21) The Gibbs energies expression in the CEF per formula unit of a solution is as follows:

\[ G = \sum_i \sum_j \gamma_i^M \gamma_j^M G_{ij} - TS_C + G^E \] ........................(3)

where \( \gamma_i^M \) and \( \gamma_j^M \) represent the site fractions of constituents \( i \) and \( j \) on the \( M_2 \) and \( M_1 \) sublattices, \( G_{ij} \) is the Gibbs energy of an "end-member", \( (i)^M(j)^M \text{SiO}_4 \) in which the \( M_2 \) and \( M_1 \) sublattices are occupied only by \( i \) and \( j \) cations respectively, \( C \) is the configurational entropy assuming random mixing on each sublattice given by:

\[ S_C = -R \left( \sum_i \gamma_i^M \ln \gamma_i^M + \sum_j \gamma_j^M \ln \gamma_j^M \right) \] ........................(4)

and \( G^E \) is the excess Gibbs energy given by:

\[ G^E = \sum_i \sum_j \sum_k \gamma_i^M \gamma_j^M \gamma_k^M L_{ij} + \sum_i \sum_j \sum_k \gamma_i^M \gamma_j^M \gamma_k^M L_{ij} \] ........................(5)

where \( L_{ij} \) and \( L_{ijk} \) are interaction energies between cations...
\[ i \text{ and } j \text{ on one sublattice when the other sublattice is occupied only by cation } k. \]

For the olivine solution, there are four end-member Gibbs energies \( G_{CC}, G_{MM}, G_{CM} \) and \( G_{MC} \) (where \( C \) and \( M \) denote \( \text{Ca}^{2+} \) and \( \text{Mn}^{2+} \), respectively). \( G_{CC} \) is equal to \( G^\circ(\text{Ca}_2\text{SiO}_4) \) which is the Gibbs energy of stoichiometric \( \text{Ca}_2\text{SiO}_4 \) and \( G_{MM} \) is equal to \( G^\circ(\text{Mn}_2\text{SiO}_4) \) which is the Gibbs energy of stoichiometric tephroite (\( \text{Mn}_2\text{SiO}_4 \)). Both of these Gibbs energies have been optimized previously.\(^{12}\)

The Gibbs energies \( G_{CM} \) and \( G_{MC} \) are model parameters which were optimized in the present study. However, rather than considering these parameters directly, it is more physically meaningful to consider the linear combinations:

\[
\begin{align*}
I_{CM} &= G_{CC} + G_{MM} - 2G_{CM} \quad \cdots \cdots (6) \\
A_{CM:CM} &= G_{CC} + G_{MM} - G_{CM} - G_{MC} \quad \cdots \cdots (7)
\end{align*}
\]

\( I_{CM} \) has the physical significance of being equal to the energy change of the site exchange reaction when \( \text{Ca}^{2+} \) and \( \text{Mn}^{2+} \), occupying \( M_2 \) and \( M_1 \) sites respectively, change places. The linear combination \( A_{CM:CM} \) similarly has physical significance as the energy change of the “reciprocal exchange reaction” among end-members, which is typically close to zero. Setting \( A_{CM:CM} \) equal to zero is equivalent to assuming that the sum of the energies of a second-nearest-neighbor \( \text{Ca}(M_2) - \text{Mn}(M_1) \) pair bond and a \( \text{Mn}(M_2) - \text{Ca}(M_1) \) pair bond is equal to the sum of the energies of a \( \text{Ca}(M_1) - \text{Ca}(M_2) \) and a \( \text{Mn}(M_1) - \text{Mn}(M_2) \) pair bond. Such a symmetrical assumption seems reasonable. For other olivine solutions, this term has been found empirically to be close to zero.\(^{37}\) Thus, in this study, \( A_{CM:CM} \) was set to be zero. The Gibbs energies and optimized parameters are listed in Table 1.

2.3. Wollastonite, Rhodonite, \( \alpha \)-\( \text{Ca}_2\text{SiO}_4 \) and \( \alpha' \)-\( \text{Ca}_2\text{SiO}_4 \) Solid Solutions

Manganese can substitute for calcium in wollastonite, \( \text{CaSiO}_3 \), which has a silicate chain structure, and similarly in \( \alpha \)- and \( \alpha' \)-\( \text{Ca}_2\text{SiO}_4 \). On the other hand, only a relatively limited amount of calcium can substitute for manganese in rhodonite, \( \text{MnSiO}_3 \). A simple random mixing model with a polynomial expansion of the excess Gibbs energy is used for these solutions:

\[
G = (G^\circ\text{A}_X + G^\circ\text{B}_X) + nRT(X_A \ln X_A + X_B \ln X_B) + G^E \quad \cdots \cdots (8)
\]

\[
G^E = \sum q_{AB}^E(X_A)(X_B)^{\prime} \quad \cdots \cdots (9)
\]

where \( G \) is the Gibbs energy per formula unit of a solution (see Table 1), \( G^\circ\text{A}_X \) and \( G^\circ\text{B}_X \) are the Gibbs energies of the pure end-members, \( G^E \) is the excess Gibbs energy, \( X_A \) and \( X_B \) are mole fractions of end-members, \( q_{AB}^E \) are the model parameters, \( n=1 \) for wollastonite s.s. and rhodonite s.s., and \( n=2 \) for the \( \alpha \)- and \( \alpha' \)-\( \text{Ca}_2\text{SiO}_4 \) solutions. Optimized model parameters are listed in Table 1.

2.4. Monoxide Solid Solution

A monoxide solid solution exists in the \( \text{CaO} – \text{MnO} \) binary system. Solid \( \text{CaO} \) and \( \text{MnO} \) exhibit complete mutual solubility. The model parameters were taken from the previous study by Wu et al.\(^{11}\)

2.5. Stoichiometric Compounds

Pseudowollastonite (\( \text{CaSiO}_3 \)), hattrurite (\( \text{Ca}_3\text{SiO}_4 \)), rankinite (\( \text{Ca}_3\text{Si}_2\text{O}_7 \)), quartz (\( \text{SiO}_2 \)), tridymite (\( \text{SiO}_2 \)), cristobalite (\( \text{SiO}_2 \)), \( \text{Ca}_3\text{Al}_2\text{O}_6 \), \( \text{Ca}_3\text{Al}_2\text{O}_7 \), \( \text{Ca}_3\text{Al}_2\text{O}_{19} \), corundum (\( \text{Al}_2\text{O}_3 \)) and galaxite (\( \text{MnAl}_2\text{O}_4 \)) were considered as stoichiometric compounds because no noticeable solubilities in these compounds have been observed in the \( \text{CaO} – \text{MnO} – \text{SiO}_2 \) and \( \text{CaO} – \text{MnO} – \text{Al}_2\text{O}_3 \) systems. Optimized Gibbs energies of these compounds and are given in Refs. 3), 4), 11) and 12).

3. Evaluation/Optimization

3.1. \( \text{CaO} – \text{MnO} – \text{SiO}_2 \) System

The calculated ternary liquidus surface (back-calculated from the optimized model parameters) is shown in Fig. 1. Glasser\(^{22}\) investigated the phase diagram of the

Fig. 1. Liquidus surface of the \( \text{CaO} – \text{MnO} – \text{SiO}_2 \) system at 1 bar pressure calculated from optimized model parameters. Temperatures in °C.
CaO–MnO–SiO₂ ternary system comprehensively at temperatures below 1600°C under reducing atmospheres (P\textsubscript{O2}/P\textsubscript{H2} ≤ 10). Samples were equilibrated at the desired temperature and quenched. The equilibrium phases were then identified, mainly by standard petrographic and X-ray diffraction techniques. Glasser also confirmed, by chemical analysis, that manganese exists mainly in the divalent state.

Ten primary phase fields were reported: tridymite (SiO₂), cristobalite (SiO₂), pseudowollastonite (CaSiO₃), rankinite (Ca₃Si₂O₇), wollastonite s.s., rhodonite s.s., α-Ca\textsubscript{2}SiO₄ s.s., pseudowollastonite, olivine s.s. and monoxide s.s. No ternary compounds were found. From X-ray lattice parameter measurements, Glasser concluded that there is no noticeable solubility of Mn\textsuperscript{2+} in rankinite and hatrurite. Although he showed a speculative hatrurite primary field in his phase diagram, he mentioned that no experimental evidence for this primary phase region was found. As can be seen in Fig. 1, no primary phase region for hatrurite was calculated in the present study. As shown in Table 2, the calculated critical points agree with those deduced by Glasser well within experimental error limits.

**Figure 2** shows the calculated primary phase regions along with experimental points of Glasser.\(^{25}\) In order to reproduce the reported phase diagram, one small ternary model parameter was introduced for the liquid phase. The calculations are in good agreement with the experimental data except for the α-Ca\textsubscript{2}SiO₄ s.s. primary region which will be discussed below.

Uchida *et al*.\(^{23}\) equilibrated Cu–Mn alloys with CaO–MnO–SiO₂ oxide mixtures under controlled CO–CO\textsubscript{2} atmospheres at 1400°C. The liquidus compositions coexisting with monoxide solid solutions were determined by chemical analysis, and activities of MnO were calculated from the known activity coefficients of Mn in Cu–Mn alloys and the oxygen partial pressure.

**Figure 3** shows the calculated isothermal section of the CaO–MnO–SiO₂ system at 1400°C. Dashed lines are tie-lines in two-phase regions.

will be discussed below.

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**Figure 4** shows the calculated phase diagram of the Ca\textsubscript{2}SiO₄–Mn\textsubscript{2}SiO₄ orthosilicate section along with the experimental data reported by Glasser.\(^{24}\) Ca\textsubscript{2}SiO₄ and Mn\textsubscript{2}SiO₄ form an olivine solid solution. Kallenberg\(^{25}\) and Toklody\(^{26}\) first investigated parts of this section. Greer\(^{27}\)

### Table 2. Special points involving the liquid in ternary systems

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Liquid Composition (Weight %)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1352</td>
<td>30.0 11.0 59.0</td>
<td>L = PW + WOLL + SiO₂ (tridymite)</td>
</tr>
<tr>
<td>Calc 1352</td>
<td>30.2 12.3 57.5</td>
<td></td>
</tr>
<tr>
<td>Exp 1460</td>
<td>33.0 17.0 50.0</td>
<td>L = PW + WOLL (mutatis mutandis)</td>
</tr>
<tr>
<td>Calc 1391</td>
<td>32.1 18.1 49.8</td>
<td></td>
</tr>
<tr>
<td>Exp 1375</td>
<td>34.0 34.0 32.0</td>
<td>L = α-Ca\textsubscript{2}SiO₄ (orthorhombic)</td>
</tr>
<tr>
<td>Calc 1375</td>
<td>32.4 35.3 32.3</td>
<td></td>
</tr>
<tr>
<td>Exp 1375</td>
<td>37.5 43.0 29.5</td>
<td>L = OL + WOLL (minimum liquidus temperature)</td>
</tr>
<tr>
<td>Calc 1375</td>
<td>38.0 42.0 20.0</td>
<td></td>
</tr>
<tr>
<td>Exp 1202</td>
<td>22.3 41.5 36.2</td>
<td>L = RH + SiO₂ (tridymite) + WOLL</td>
</tr>
<tr>
<td>Calc 1240</td>
<td>4.0 58.0 40.0</td>
<td></td>
</tr>
<tr>
<td>Calc 1228</td>
<td>4.4 56.5 39.1</td>
<td></td>
</tr>
<tr>
<td>Exp 1271</td>
<td>4.8 48.5 46.7</td>
<td>L = OL + MONO + OL (local minimum temperature)</td>
</tr>
<tr>
<td>Calc 1271</td>
<td>4.8 48.7 46.5</td>
<td></td>
</tr>
<tr>
<td>Exp 1215</td>
<td>4.0 58.0 40.0</td>
<td>L = α-Ca\textsubscript{2}SiO₄ + ε-Ca\textsubscript{2}SiO₄</td>
</tr>
<tr>
<td>Calc 1245</td>
<td>5.2 44.9 44.7</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2. Special points involving the liquid in ternary systems**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Liquid Composition (Weight %)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc 1379</td>
<td>61.6 7.4 31.0</td>
<td>L = Al\textsubscript{2}O\textsubscript{3} + Ca\textsubscript{2}Al\textsubscript{2}O\textsubscript{6} + Mn\textsubscript{2}Al\textsubscript{2}O\textsubscript{6}</td>
</tr>
<tr>
<td>Calc 1682</td>
<td>69.6 15.9 14.5</td>
<td>L = Ca\textsubscript{2}Al\textsubscript{2}O\textsubscript{6} + Mn\textsubscript{2}Al\textsubscript{2}O\textsubscript{6}</td>
</tr>
<tr>
<td>Calc 1480</td>
<td>59.9 28.1 12.9</td>
<td>L = Ca\textsubscript{2}Al\textsubscript{2}O\textsubscript{6} + Mn\textsubscript{2}Al\textsubscript{2}O\textsubscript{6}</td>
</tr>
<tr>
<td>Calc 1395</td>
<td>44.6 27.4 28.0</td>
<td>L = Mn\textsubscript{2}SiO\textsubscript{4} + Al\textsubscript{2}O\textsubscript{3} (monoxide s.s.)</td>
</tr>
<tr>
<td>Calc 1287</td>
<td>45.8 46.4 7.8</td>
<td>L = Mn\textsubscript{2}SiO\textsubscript{4} + Al\textsubscript{2}O\textsubscript{3} (monoxide s.s.)</td>
</tr>
</tbody>
</table>

\*L: Liquid slag, PW: Pseudowollastonite (Ca₅Si₃O₁₀), WOLL: Wollastonite s.s., CΣ₂: Ca₃Si₃O₁₀ s.s., α: α-Ca₃Si₂O₇ s.s., λ: λ-Ca\textsubscript{2}SiO₄ s.s., OL: Olivine s.s., RH: Rhodonite s.s., MONO: Monoxide s.s.

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found, from XRD and refractive index measurements, that Ca$_2$SiO$_4$–Mn$_2$SiO$_4$ mixtures have the same crystal structure across the entire composition range. Goldschmidt and Rait$^{28}$ reported that they synthesized a "manganese merwinit" (Ca$_3$MnSi$_2$O$_8$) compound by heating to 1 400°C in a hydrogen atmosphere. However, Glasser$^{24}$ could not find this compound. Several studies$^{29}$–$^{31}$ reported the existence of a glaucochroite (CaMnSiO$_4$) compound, which was later found by O'Daniel et al.$^{32}$ to be part of the olivine solution. Many other binary olivine solutions (Ca$_2$SiO$_4$–Fe$_2$SiO$_4$, $^{33,34}$Fe$_2$SiO$_4$–Mg$_2$SiO$_4$, $^{35}$Mn$_2$SiO$_4$–Fe$_2$SiO$_4$, $^{36}$) exhibit complete miscibility at all compositions. Thus, in the present study, no compounds were considered in the orthosilicate section.

In order to model the olivine solid solution, the cation distribution of Ca$^{2+}$ and Mn$^{2+}$ between M$_2$ and M$_1$ sites must be known. However, no experimental studies of this have been reported. Therefore, the cation distribution was estimated as follows. The distribution of cations A$^{2+}$ and B$^{2+}$ between the sublattices can be expressed by the following site exchange reaction:

$$[B]_{M1} = [A]_{M2}$$

$$[A]_{M1} = [B]_{M2}$$

$$[B]_{M2} + [A]_{M1}$$

These site exchange reactions can be approximated as:

$$K_D = \frac{[X_B]_{M1}[X_A]_{M2}}{[X_A]_{M1}[X_B]_{M2}}$$

where the are [X$_i$] the site fractions.

As can be seen in Fig. 5, Jung$^{27}$ observed a linear relationship between $\ln K_D$ and the ratio of cationic radii$^{29}$ for various olivine solutions. From this relationship, $K_D$ of the present olivine solution is estimated as 0.0299 at 1 000°C. In order to reproduce this cation distribution and the measured phase diagram, optimized values of the $\alpha_{CM}$ parameter and one excess parameter for the olivine solution were obtained (Table 1).

The phase diagram for the orthosilicate section as drawn by Glasser$^{24}$ is shown in Fig. 6. This diagram is thermodynamically incorrect near the minimum at 1 240°C. Also, the change in liquidus slope at point F can be shown to be inconsistent with the enthalpy of the $\alpha\rightarrow\alpha'$ phase transformation of Ca$_2$SiO$_4$.$^{24,25}$ The calculated section in Fig. 4 reproduces Glasser's data within error limits and is, of course, thermodynamically consistent.

From the optimized model parameters required to reproduce the liquidus/solidus, a region of immiscibility in the olivine solid solution is predicted as shown in Fig. 4. This requires experimental verification. Similar miscibility gaps are observed in the Ca$_2$SiO$_4$–Fe$_2$SiO$_4$,$^{33,34}$ and Ca$_2$SiO$_4$–Mg$_2$SiO$_4$,$^{37}$ olivine solutions.

The calculated liquidus of $\alpha'$-Ca$_2$SiO$_4$ s.s. in Fig. 4 extends to much lower Mn$_2$SiO$_4$ concentration than in Glasser's diagram (Fig. 6). This is the principal reason for the aforementioned disagreement regarding the primary phase region of $\alpha'$-Ca$_2$SiO$_4$ s.s. in Fig. 2.

It can be seen in Fig. 4 that Glasser$^{24}$ reported that a small amount of the monoxide phase appeared in the orthosilicate section. We found this impossible to reproduce with reasonable model parameters while simultaneously reproducing the experimental data in Fig. 3. However, if we calculate a phase diagram section at a silica mole fraction (rather than on the orthosilicate section), then Glasser's observations are very closely reproduced, as shown in Fig. 7.

That is, the discrepancy can be explained by a very small deviation of the experimental compositions from the or-

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**Fig. 4.** Calculated phase diagram of the Ca$_2$SiO$_4$–Mn$_2$SiO$_4$ orthosilicate section.

**Fig. 5.** Estimated relationship between cation distribution and cation radius ratio in olivine solid solutions at 1 000°C. The cation radius of A is bigger than that of B.
thosilicate section.

**Figure 8** shows the optimized phase diagram for the CaSiO$_3$–MnSiO$_3$ metasilicate section along with experimental data of Glasser. This section does not constitute a true pseudo-binary join since tridymite appears. Glasser investigated the phase equilibria in this section by a classical quenching technique followed by optical and XRD phase identification. He reported two solid solutions, wollastonite s.s. and rhodonite s.s.. Mikirticheva et al., from measurements of refractive index, also reported a bustamite solid
solution, which is very similar to wollastonite in structure. However, the composition range of bustamite s.s. was not determined, and bustamite s.s. was not considered in the present optimization.

The calculated liquidus of pseudowollastonite in Fig. 8 and the experimental data do not agree. In order to reproduce the experimental points, a considerable solubility of Mn$_2$O$_3$ in pseudowollastonite must be postulated. However, the solubility estimated from refractive index measurements is less than 2 wt%, which is within the analytical uncertainty. Also no noticeable solubility of Fe$_2$O$_3$ and Mg$_2$O has been observed in pseudowollastonite. Hence, pseudowollastonite was regarded as a stoichiometric compound in the present study, and the reported liquidus points are most likely in error since they do not respect the limiting liquidus slope rule.

Ding and Olsen [45] studied the equilibria between CaO–MnO–SiO$_2$ slags and C-saturated or SiC-saturated Mn–Si–C alloys held in a graphite crucible. After equilibration and quenching, the compositions of the slag and metal phases were determined by EPMA and chemical analysis respectively. Their results are compared in Fig. 9 with the model calculations which are presented as curves showing the slag compositions in equilibrium with Mn–Si–C alloys of constant weight percent Si. The agreement is, in general, good. In the calculations, the thermodynamic properties of the alloys were calculated using the optimized database of Tang and Olsen [46].

Activities of MnO in CaO–MnO–SiO$_2$ liquid solutions were measured by Mehta and Richardson [47] and by Abraham, Davies and Richardson [48] using a gas/slag/Pt alloy equilibration technique under reducing atmospheres. After equilibration, the content of Mn in the Pt alloy and the composition of the slag were determined by chemical analysis. The activities of MnO were then calculated from the known Henrian activity coefficient of Mn in Pt and the controlled oxygen partial pressure. As can be seen in Figs. 10(a) and 10(b), the calculated activities of MnO (solid standard state) are in reasonable agreement with the experimental data at 1 500°C and 1 650°C, except at low MnO.
contents ($\alpha_{\text{MnO}}$ < 0.1) where the calculated activities are generally higher than the observed. However, as just shown in Fig. 9, the model calculations are in agreement with the results of Ding and Olsen\textsuperscript{45} in this concentration range.

Furthermore, measurements by the same authors\textsuperscript{48} in CaO-MnO-SiO\textsubscript{2} slags at low Al\textsubscript{2}O\textsubscript{3} (6.7 %) and low MnO contents are also in agreement with the model calculations.\textsuperscript{2}
Activities of CaO and SiO$_2$ at 1600°C are calculated in Figs. 11(a) and 11(b), from the Modified Quasichemical Model with the optimized model parameters.

### 3.2. CaO–MnO–Al$_2$O$_3$ System

There are no reported studies of the phase diagram of the CaO–MnO–Al$_2$O$_3$ system. Figure 12 shows the predicted liquidus surface. The “asymmetric approximation” with Al$_2$O$_3$ as the “asymmetric component” was used to calculate the Gibbs energy of the ternary liquid from the optimized parameters of the binary sub-systems. No additional ternary parameters were used. No ternary compounds or ternary solid solutions were considered because none have been reported. The predicted invariant points are listed in Table 2.

Figures 14(a), 14(b) and 14(c) show the activities of CaO, MnO and Al$_2$O$_3$ at 1600°C in CaO–MnO–Al$_2$O$_3$ liquid solutions calculated from the Modified Quasichemical Model using the optimized binary model parameters.

**Fig. 13.** Calculated activities of MnO in CaO–MnO–Al$_2$O$_3$ liquid solutions. (wt% CaO/wt% Al$_2$O$_3$) = A: 1/1, B: 4/6, C: 3/7, D: 2/8, E: 0/1 (MnO–Al$_2$O$_3$ binary system). Calculated line A and data from Morita et al. represent the activity of MnO at 1600°C while others are at 1650°C.

**Fig. 14.** Calculated iso-activity lines of (a) CaO, (b) MnO and (c) Al$_2$O$_3$ in CaO–MnO–Al$_2$O$_3$ liquid solutions calculated from the Modified Quasichemical Model using the optimized binary model parameters.
4. Conclusions

A complete review and critical evaluation of all available phase equilibrium and thermodynamic data for the CaO–MnO–SiO₂ and CaO–MnO–Al₂O₃ systems were carried out, and a database of optimized model parameters was prepared in order to thermodynamically model the complete CaO–MnO–SiO₂–Al₂O₃ system at 1 bar total pressure using the FactSage® thermochemical computing system. All reliable experimental data are reproduced within experimental error limits by a very few model parameters. The liquidus surface of the CaO–MnO–Al₂O₃ system, which has not been measured, has been predicted. Moreover, phase equilibria between CaO–MnO–SiO₂ liquid slags and manganese alloys have been calculated, with good agreement obtained between calculation and experimental data. With the present optimized database, it is possible to calculate any phase diagram section of the CaO–MnO–SiO₂ and CaO–MnO–Al₂O₃ systems at all compositions and temperatures. In a subsequent article, the study will be extended to the evaluation and prediction of phase equilibria and thermodynamic properties of the CaO–MnO–SiO₂–Al₂O₃ quaternary system.

By coupling the presently developed database with other evaluated FactSage® databases for metallic solutions, gases, etc., complex slag/metal/solid/gas equilibria can be computed.

Acknowledgements

This project was supported by POSCO (Pohang Steel Co., Korea) and a CRD grant from the Natural Sciences and Engineering Research Council of Canada in collaboration with the following: Alcoa, Corning, Dupont, INCO, Mintek, Noranda, Norsk Hydro, Pechiney, Rio Tinto, Schott Glass, Shell, Sintef, St.-Gobain Recherche, Teck Cominco and IIS Materials. We also thank Dr. K. Tang (Sintef, Norway) for supplying the ferromanganese alloy database and unpublished experimental references.

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