Phase Equilibria in High MgO Ferro-manganese and Silico-manganese Smelting Slags

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Liquidus isotherms and phase equilibria have been determined experimentally for a pseudo-ternary section of the form “MnO”–(CaO–MgO)–(SiO2–Al2O3) with a fixed Al2O3/SiO2 weight ratio of 0.17 and MgO/CaO weight ratio of 0.17 for temperatures in the range 1 473–1 673 K. The primary phase fields present for the section investigated include manganosite (Mn,Mg,Ca)O; dicalcium silicate α2(Ca2Mg3Al2Si7O22); merwinite 3CaO·(2Mg2Ca2Si2O5); wollastonite [Ca2(Mg2Ca2Si2O5)]; diopside [Ca2Mg3Al2Si2O8]; tridymite (SiO2); tephroite [2(Mn2Mg)2O·SiO2]; rhodonite [Mn2O·SiO2]; and melilite [2CaO·(MgO·MnO·Al2O3)·2SiO2]. The liquidus temperatures relevant to ferro-manganese and silico-manganese smelting slags have been determined. The liquidus temperature is shown to be principally dependent on the modified basicity weight ratio (CaO+MgO)/(SiO2+Al2O3) at low MnO concentrations, and dependent on the mole ratio (CaO+MgO+2MnO)/(SiO2+Al2O3) at higher MnO concentrations.

KEY WORDS: slag; equilibria; “MnO”–CaO–MgO–SiO2–Al2O3; liquidus.

1. Introduction

The ternary system CaO–“MnO”–SiO2 has been widely used to describe the general chemical behaviour of ferro-manganese and silico-manganese smelting slags. However, many ores contain significant concentrations of Al2O3 and MgO, and the influence of these components cannot be ignored if optimum conditions are to be achieved in industrial practice.

Experimental determination of high temperature phase equilibria in Mn-containing systems under reducing conditions is made more difficult by the vaporisation of manganese during equilibration. Ding and Olsen2) have measured liquidus temperatures in the systems “MnO”–SiO2, “MnO”–SiO2–CaO, “MnO”–SiO2–Al2O3 and “MnO”–CaO–SiO2–Al2O3 in equilibrium with Mn–Si–C alloy. The compositions of the quenched slag samples were determined by X-ray fluorescence and the liquidus were determined by metallographic examination of quenched specimens.

Experimental determination of high temperature phase equilibria and liquidus temperatures in the “MnO”–SiO2–Al2O3 system has been recently carried out by Roghani et al.3) Subsequently all data have been reviewed and evaluated and an optimised thermodynamic database for this system has been developed.4) In the system “MnO”–Al2O3–CaO–SiO2 the liquidus has been determined experimentally in a number of studies using equilibration, quenching and electron probe X-ray microanalysis (EPMA). The liquidus compositions at 1 723, 1 773 and 1 823 K have been measured in the primary phase field of manganosite, MnO, for Al2O3/SiO2 weight ratios of 0.25 and 0.5.5) Liquidus temperatures have also been measured in the system “MnO”–Al2O3–CaO–SiO2 for 6 and 12 wt% MnO sections.6) The phase equilibria and liquidus isotherms for temperatures between 1 473 and 1 673 K have been systematically determined in the system “MnO”–Al2O3–CaO–SiO2 for Al2O3/SiO2 weight ratios of 0.41, 0.55 and 0.65.7) In these later studies the results have been presented as pseudo-ternary sections of the quaternary in the form of “MnO”–CaO–(SiO2/Al2O3). This form of representation with “MnO” in one apex provides information that is useful to industrial ferro-manganese production practice since the changing phase equilibria can be readily followed as manganese is removed from the slag.

The chemistries of the ferro-manganese and silico-manganese slags are more accurately described by the five component system “MnO”–CaO–MgO–SiO2–Al2O3. The liquidus temperatures have been measured in the system “MnO”–CaO–MgO–SiO2–Al2O3 at 1 723 and 1 823 K for Al2O3/SiO2 weight ratios of 0.41, 0.55 and 0.65.8) In these later studies the results have been presented as pseudo-ternary sections of the quaternary in the form of “MnO”–CaO–(SiO2/Al2O3). This form of representation with “MnO” in one apex provides information that is useful to industrial ferro-manganese production practice since the changing phase equilibria can be readily followed as manganese is removed from the slag.
5–15 wt%; SiO$_2$, 27–58 wt%; Al$_2$O$_3$, 5 wt%; FeO negligible (~0.5 wt%). Extensive vaporisation or “boiling” of manganese was observed but it was not possible to measure the slag bulk compositions after the experiments. Solid phases were not identified and the compositions of the solid primary phases were not measured in this study.$^{39}$ The liquidus data was presented for a range of nominal compositions as a function of bulk MnO concentration, (CaO+MgO)/SiO$_2$ ratio and CaO/MgO ratio.

In a previous study$^{39}$ it has been found that significant MgO is present in manganosite. It is also to be expected, given the similarity in ionic size, that MgO can be dissolved in the Mn-containing silicate phases in the system “MnO”–CaO–MgO–SiO$_2$–Al$_2$O$_3$. However, there are no data available on phase equilibria on these solid solutions. The compositions of the solid solutions and coexisting solid and liquid phases will be important data for development of thermodynamic databases for this system.

South African manganese ores and concentrates are characterised by high MgO and low Al$_2$O$_3$ contents. The compositions of the slags produced during the production of ferro-manganese and silico-manganese from South African manganese ores and concentrates are the focus of the present investigation since there are currently no data available on the phase equilibria and liquidus temperatures in the composition range relevant to these slags.

2. Experimental Procedure

The experimental method used in the present study involves high temperature equilibration, quenching and electron probe X-ray microanalysis (EPMA). The experimental procedure is similar to those described in previous publications.$^{10,11}$ During high temperature equilibration the “MnO” and SiO$_2$ concentrations in the slag change because of vaporisation and reactions with Mn–Si alloy present in the system. However, in the present study these changes do not affect the final results since the measurements of the phase compositions are carried out after rather than before the experiments. This technique enables the liquidus of the slags to be accurately characterised experimentally.

Appropriate selection of the form of pseudo-ternary sections is important for efficient research and industrial application of this experimental information. In the present study of the system “MnO”–CaO–MgO–SiO$_2$–Al$_2$O$_3$ a pseudo-ternary section has been constructed. The apexes of the pseudo-ternary section are “MnO”, (CaO+MgO) and (SiO$_2$+Al$_2$O$_3$). The Al$_2$O$_3$/SiO$_2$ weight ratio is fixed at 0.17 and MgO/CaO weight ratio of 0.17 has been selected in the current study. These ratios are close to those in the slags in ferro-manganese and silicon-manganese production in some South African Smelters. In this way the systematic variation of liquidus with the modified basicity of the slag, i.e., (CaO+MgO)/(SiO$_2$+Al$_2$O$_3$) ratio can be readily examined.

A series of synthetic master slags were prepared from high purity (99+%) MgO, SiO$_2$, Al$_2$O$_3$ and CaCO$_3$ powders. The mixtures were pelletised and placed in a platinum crucible and heated in air at 1873 K for several hours. The quenched master slags were ground and mixed with MnO and Mn–Si alloy to obtain final mixtures. The Mn–Si alloy was prepared by mixing Mn and Si powders with mole ratio of Mn : Si = 3 : 1 and heating under argon gas in a carbon crucible at 1473 K for 2 h. Mn–Si alloy powder was added to the slag to ensure that the manganese was present predominantly in its lowest oxidation state Mn$^{2+}$. The Mn : Si ratio in the alloy was selected after preliminary experiments indicated that, for the range of compositions studied, the extents of the reactions between the alloy and the slag were minimum. Sufficient alloy powder was added to ensure that alloy is still present dispersed throughout the sample after the experiment was completed; ensuring local equilibrium between the alloy and the slag was achieved.

Approximately 0.3 g of final mixture were pelletised and wrapped into an envelope of Mo foil. Equilibration experiments were carried out in an atmosphere of high purity Ar gas in a vertical recrystallised alumina reaction tube heated by SiC elements. The mixture, wrapped in a Mo envelope, was suspended in a Mo dish using a Kanthal wire. The sample was equilibrated at a predetermed temperature for times from 1 to 16 h depending on the composition and temperature, and then quenched into ice-cooled water.

The quenched samples were mounted and polished for metallographic examination. A JEOL 8800L Electron Probe Microanalyser (EPMA) with Wave Length Dispersive detectors was used for measurements of the phase compositions. The standards used for EPMA include alumina (Al$_2$O$_3$) for Al, magnesia (MgO) for Mg, spessartine (Mn$_3$Al$_2$Si$_3$O$_{12}$) for Mn and wollastonite (CaSiO$_3$) for Ca and Si. These standards were provided by Charles M Taylor Co., Stanford, California, USA. The analysis was conducted at an accelerating voltage of 15 kV and a probe current of 15 nA. The ZAF correction procedure supplied with the electron probe was applied. The average accuracy of the EPMA measurements is within ±1 wt%. Under experimental conditions used in the present study there may be both Mn$^{2+}$ and Mn$^{3+}$ present in the samples. However, only the metal cation ratios can be measured using the EPMA; the phase compositions were recalculated to oxides on the assumption that all manganese is present as Mn$^{2+}$. Although it is possible to measure the compositions of the oxide phase unfortunately it has not been possible to determine the mean compositions of the fine dispersed alloy in the quenched samples.

An important feature to note for the systems under investigation is that the compositions of the solid primary phases do not have the same Al$_2$O$_3$/SiO$_2$ and MgO/CaO ratios as the liquid present in the pseudo-ternary section. The precipitation of these crystals from the melt will result in the selective removal of the components from the slag phase. This means that on crystallisation the compositions of the remaining liquids will move out of the selected section. The greater the proportion of the solid phase formed, the further the liquid composition is moved away from the selected section. The approach that has been adopted in the present study is to select possible conditions where a low fraction of solid phase occurs. However, for two reasons it is difficult to control the fraction of solid phase at a low value. a) The compositions of the solid phases (e.g. melilite and dicalcium silicate) are relatively close to the liquid compositions. Small changes in bulk composition can result in a large change in proportions of the liquid and solid phases, for example, from one...
Table 1. Experimental results in system CaO–MgO–MnO–Al$_2$O$_3$–SiO$_2$ with Al$_2$O$_3$/SiO$_2$ weight ratio of 0.17 and MgO/CaO weight ratio of 0.17 in equilibrium with Mn–Si alloy.

| Exp. number | Temperature (°C) | Phases | Composition (wt%) | CaO–MgO–Al$_2$O$_3$–SiO$_2$ |
|-------------|-----------------|--------|-------------------|-----------------------------|
| 388         | 1473 liquid     | 18.6   | 3.2               | 28.7                         |
| 36         | 1523 liquid     | 26.1   | 3.6               | 0.0                          |
| 141        | 1523 liquid     | 27.7   | 0.8               | 0.0                          |
| 142        | 1523 liquid     | 30.5   | 0.0               | 0.0                          |
| 233        | 1573 liquid     | 34.2   | 5.7               | 9.1                          |
| 310        | 1573 liquid     | 30.7   | 2.2               | 20.1                         |
| 319        | 1573 liquid     | 39.8   | 6.9               | 7.0                          |
| 243        | 1573 liquid     | 41.4   | 6.7               | 7.0                          |
| 243        | 1573 liquid     | 35.8   | 31.2              | 6.3                          |
| 402        | 1573 liquid     | 30.1   | 0.0               | 0.0                          |
| 14         | 1573 liquid     | 41.5   | 7.0               | 7.7                          |
| 4         | 1673 liquid     | 42.5   | 6.1               | 7.0                          |
| 9          | 1473 liquid     | 24.4   | 3.8               | 0.0                          |
| 10         | 1573 liquid     | 24.4   | 3.6               | 0.0                          |
| 306        | 1623 liquid     | 18.8   | 3.0               | 44.2                         |
| 320        | 1623 liquid     | 30.7   | 3.4               | 0.8                          |
| 320        | 1623 liquid     | 30.7   | 3.4               | 0.8                          |
| 434        | 1623 liquid     | 0.0    | 0.0               | 61.6                         |
| 294        | 1623 liquid     | 13.8   | 1.8               | 51.0                         |
| 293        | 1623 liquid     | 13.4   | 2.0               | 53.0                         |
| 305        | 1623 liquid     | 18.4   | 3.0               | 45.0                         |
| 356        | 1473 liquid     | 27.3   | 4.8               | 15.1                         |
| 390        | 1473 liquid     | 25.4   | 4.6               | 20.2                         |
| 390        | 1473 liquid     | 30.5   | 3.1               | 12.0                         |
| 390        | 1473 liquid     | 30.5   | 3.1               | 12.0                         |
| 390        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 390        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 390        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
| 357        | 1473 liquid     | 41.0   | 11.5              | 0.0                          |
| 357        | 1473 liquid     | 33.6   | 5.5               | 5.3                          |
| 357        | 1473 liquid     | 39.8   | 9.4               | 7.6                          |
| 357        | 1473 liquid     | 42.2   | 4.2               | 0.0                          |
containing significant volume fraction of melilite to one where only liquid phase is present. b) A number of reactions always occur during high temperature equilibration including:

\[
\begin{align*}
2\text{Mn(metal)} + \text{H}_2\text{O(gas)} &\rightarrow 2\text{MnO(slag)} + \text{Si(metal)} \\
\text{Si(metal)} + \text{H}_2\text{O(gas)} &\rightarrow \text{SiO}_2\text{(slag)} + \text{Mn(metal)} \\
\text{Si(metal)} + 2\text{MnO(slag)} &\rightarrow \text{SiO}_2\text{(slag)} + 2\text{Mn(metal)} \\
\text{Mn(metal)} + \text{H}_2\text{O(gas)} &\rightarrow \text{Mn(gas)} + \text{SiO}_2\text{(slag)} \\
\text{Si(metal)} + \text{H}_2\text{O(gas)} &\rightarrow \text{SiO}_2\text{(slag)} + \text{Mn(metal)} \\
\text{Mn(metal)} + \text{H}_2\text{O(gas)} &\rightarrow \text{Mn(gas)} + \text{SiO}_2\text{(slag)} \\
\text{Mn(metal)} + 2\text{MnO(slag)} &\rightarrow 2\text{Mn(metal)} + \text{SiO}_2\text{(slag)}
\end{align*}
\]

These reactions change the bulk composition of the oxide melt, which makes it more difficult to control the fraction of solid phases. Although experiments were carefully planned, the liquid compositions at or near to the selected ratios, in general, cannot be achieved with the first experiment. This means that experiments in these primary phase fields must be repeated several times before results on the desired pseudo-ternary sections are obtained.

3. Experimental Results

3.1. Description of the Pseudo-ternary Section

The compositions of the phases present following equilibration of the oxide/alloy mixture, measured using EPMA, are presented in Table 1. These data have been used to construct liquidus isotherms and the liquidus surface of the pseudo-ternary section “MnO–(CaO–MgO)–(SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3})” with a fixed Al\textsubscript{2}O\textsubscript{3}/Si\textsubscript{2}O weight ratio of 0.17 and MgO/CaO weight ratio of 0.17.

Figure 1 shows the experimentally determined liquidus points with compositions having the appropriate Al\textsubscript{2}O\textsubscript{3}/Si\textsubscript{2}O and MgO/CaO ratios. The remaining data in Table 1 are provided since these are
valuable for subsequent thermodynamic modelling of this system. The isotherm surface of the pseudo-ternary section for the five-component system are shown in Fig. 2. The liquidus isotherms at 1473, 1523, 1573, 1623 and 1673 K have been determined.

The experimentally determined phase boundaries are marked with thick full lines. The boundaries marked with dashed lines indicate the approximate positions. Experimental data were obtained in all primary phase fields, including the pseudo-binary joins (CaO–MgO)–(SiO2–Al2O3) and “MnO”–(SiO2–Al2O3).

The pseudo-ternary section is characterised by the presence of the following primary phase fields (see Fig. 2): Manganosite (Mn,Mg,Ca)O; dicalcium silicate α–2(Ca,Mg,Mn)O·SiO2; merwinite 3CaO·(Mg,Mn)O·2SiO2; wollastonite [(Ca,Mg,Mn)O·SiO2]; diopside (Ca,Mg,Mn,O,Al,Si)2O5·SiO2; tridymite (SiO2); tephroite [2(Mn,Mg)O·SiO2]; rhodonite [(Mn,Mg)O·SiO2] and melilite [2CaO·(MgO,MnO,Al2O3)·2(SiO2,Al2O3)].

3.2. Comparison with Other Systems

The experimental data on the liquidus obtained in the present study in the joins (CaO–MgO)–(SiO2–Al2O3) with fixed Al2O3/SiO2 weight ratio of 0.17 and MgO/CaO weight ratio of 0.17 in equilibrium with Mn–Si alloy, compositions in wt%, temperatures in K.

Fig. 1. Experimental data obtained on the liquidus of the system “MnO”–CaO–MgO–SiO2–Al2O3 with weight ratios of Al2O3/SiO2=0.17 and MgO/CaO=0.17 in equilibrium with Mn–Si alloy, compositions in wt%, temperatures in K.

To assist in the comparison of the liquidus temperatures between the ternary CaO–“MnO”–SiO2 and the pseudo-ternary system “MnO”–(CaO–MgO)–(SiO2–Al2O3) determined in the present study, the liquidus temperatures for the section at 20 wt% MnO are presented in Fig. 3. It can be seen from Fig. 3 that at low (CaO–MgO) concentrations the liquidus temperatures in the five-component system are significantly lower than those in the ternary. Between 37 and 43 wt% (CaO–MgO) the liquidus temperatures in the five-component system are slightly higher than those in the ternary. In the melilite, dicalcium silicate and tephroite primary phase fields the liquidus temperature of the slag gradually increases with increasing (CaO–MgO) concentrations. In the manganosite primary phase field the liquidus temperature increases dramatically with increasing (CaO–MgO) concentration of the slag.

In Fig. 4 the change in liquidus temperature with changing MnO concentration is plotted for (CaO–MgO)/ (SiO2–Al2O3) ratio of 0.90 to reflect the liquidus as the slags are reduced during the smelting operation. It can be seen that in the region where the MnO concentration is lower than 25 wt% the liquidus temperature in the five-com-
ponent slags does not significantly change with MnO concentration. This behaviour reflects the shape of the liquidus in Fig. 1 where the isotherms in the melilite and tephroite primary phase fields are nearly parallel to the join “MnO”–[(CaO/MgO)/(SiO2/Al2O3)] with (CaO/MgO)/(SiO2/Al2O3) ratio of 0.90. The presence of MgO in the manganosite solid solution is shown to extend the primary phase field of this phase. For MnO concentrations greater than 25 wt% the liquidus temperatures increase rapidly with increasing MnO concentration.

3.3. The Relationships between Liquidus Temperature and Basicity

Eric et al.\textsuperscript{9) reported a general trend that the liquidus temperatures of manganese smelting slags increase with increasing basicity (CaO/MgO)/SiO2 at fixed MnO concentrations. The experimental data from present study have been used to determine the relationship between liquidus temperature and basicity of the liquid phase.

Traditionally basicity of the slags are defined in terms of the weight ratio (CaO/MgO)/SiO2. Since in the current study Al2O3 is also present in the slags a modified basicity ratio (CaO/MgO)/(SiO2/Al2O3) is introduced. In Figs. 5 and 6 the liquidus temperatures are plotted against the traditional and modified basicities for Al2O3/SiO2 ratio of 0.15–0.19, MgO/CaO ratio of 0.15–0.19 and MnO concentrations in the range of 0–30 wt%. In the melilite, merwinitite, dicalcium silicate and tephroite primary phase fields the relationships between liquidus and basicity rates are ap-
approximately linear and are described by the following equations:

\[ T_{\text{liq}}(K) = 332 \times \frac{(\text{wt}\% \text{CaO} + \text{wt}\% \text{MgO})}{\text{wt}\% \text{SiO}_2} + 1258 \]  

\[ T_{\text{liq}}(K) = 376 \times \frac{(\text{wt}\% \text{CaO} + \text{wt}\% \text{MgO})}{(\text{wt}\% \text{Al}_2\text{O}_3 + \text{wt}\% \text{SiO}_2)} + 1260 \]

where: \( T_{\text{liq}} \) is liquidus temperature in K, \((\text{CaO} + \text{MgO})/\text{SiO}_2\) is the traditional basicity and \((\text{CaO} + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{SiO}_2)\) is the modified basicity. The squares of the correlation coefficient \( R^2 \) are 0.96 and 0.97 respectively for Eqs. (1) and (2).

In industrial ferro-manganese smelting practice a mole ratio of \((\text{CaO} + \text{MgO})/\text{SiO}_2\) can be used to evaluate the relationship between liquidus temperature and slag composition. It was found from the present study that for slags in the composition range of \(\text{Al}_2\text{O}_3/\text{SiO}_2\) ratio of 0.10–0.20, \(\text{MgO}/\text{CaO}\) ratio of 0.10–0.20 and \(\text{MnO}\) concentrations 20–53 wt%, the liquidus temperature is described by following equation:

\[ T_{\text{liq}}(K) = 202 \times \frac{\text{mol}\% \text{CaO} + \text{mol}\% \text{MgO} + \text{mol}\% \text{MnO}}{\text{mol}\% \text{Al}_2\text{O}_3 + \text{mol}\% \text{SiO}_2} + 1260 \]

The square of the correlation coefficient is 0.89 for Eq. (3). The experimental data used in these correlations are in the tephroite and manganosite primary phase fields.

### 3.4. Solid Solutions

Not only the liquid but also solid phase compositions have been simultaneously determined by EPMA measurements in present study. It can be seen from Table 1 that extensive solid solutions have been observed for most of the solid phases. For example, at 1 673 K (Exp. No 326) 1.9 wt% CaO, 12.5 wt% MgO and 85.4 wt% MnO are present in manganosite in equilibrium with dicalcium silicate containing 51.4 wt% CaO, 2.0 wt% MgO and 12.3 wt% MnO. At 1 623 K (Exp. No 318) 1.2 wt% CaO, 10.8 wt% MgO and 87.8 wt% MnO are present in manganosite in equilibrium with tephroite containing 34.5 wt% CaO, 7.9 wt% MgO and 23.5 wt% MnO. These data of solid solutions will be valuable for development of thermodynamic modelling.

### 4. Conclusions

The liquidus temperatures and phase relations in the system “\(\text{MnO}^+\)–(\(\text{CaO} + \text{MgO}\))–(\(\text{SiO}_2 + \text{Al}_2\text{O}_3\))” with a fixed \(\text{Al}_2\text{O}_3/\text{SiO}_2\) weight ratio of 0.17 and \(\text{MgO}/\text{CaO}\) weight ratio of 0.17 have been determined in equilibrium with Mn–Si alloy in the temperature range 1 473–1 673 K.

The phases present at the liquidus surfaces in this system include: manganosite \((\text{Mn,Mg,Ca})\text{O}\); dicalcium silicate \(\alpha-2\text{(Ca,Mg,Mn)}\text{O} \cdot \text{SiO}_2\); merwinite \(3\text{CaO} \cdot \text{(Mg,Mn)}\text{O} \cdot 2\text{SiO}_2\); wollastonite \([\text{Ca,Mg,Mn})\text{O} \cdot \text{SiO}_2]\); diopside \([\text{CaO,MgO,MnO,Al}_2\text{O}_3] \cdot \text{SiO}_2]\); tridymite \((\text{SiO}_2)\); tephroite \([2\text{(Mn,Mg)}\text{O} \cdot \text{SiO}_2]\); rhodonite \([\text{(Mn,Mg)}\text{O} \cdot \text{SiO}_2]\) and melilite \([2\text{CaO} \cdot (\text{MgO,MnO,Al}_2\text{O}_3) \cdot 2(\text{SiO}_2,\text{Al}_2\text{O}_3)]\). The liquidus temperatures and primary phase fields in the quinary system are markedly different from the system CaO–MnO–SiO$_2$ under reducing conditions. The liquidus temperature is shown to be principally dependent on the modified basicity weight ratio \((\text{CaO}/\text{MgO})/(\text{SiO}_2/\text{Al}_2\text{O}_3)\) at low \(\text{MnO}\) concentrations, and dependent on the mole ratio \((\text{CaO} + \text{MgO} + \text{MnO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)\) at higher \(\text{MnO}\) concentrations.

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REFERENCES

1) F. P. Glasser: *J. Am. Ceram. Soc.*, **45** (1962), 242.
2) W. Ding and S. E. Olsen: *Metall. Mater. Trans. B*, **27B** (1996), 5.
3) G. Roghani, E. Jak and P. Hayes: *Metall. Mater. Trans. B*, **33B** (2002), 827.
4) I.-H. Jung, Y.-B. Kang, S. A. Decterov and A. D. Pelton: *Metall. Mater. Trans. B*, **35B** (2004), 259.
5) R. Rait and S. E. Olsen: *Scand. J. Metall.*, **28** (1999), 53.
6) R. Rait and S. E. Olsen: Proc. 6th Int. Conf. on Molten Slags, Fluxes and Salts, Royal Institute of Technology, Stockholm, Sweden, (2000), paper 018.
7) G. Roghani, E. Jak and P. Hayes: *Metall. Mater. Trans. B*, **33B** (2002), 839.
8) G. Roghani, E. Jak and P. Hayes: *Metall. Mater. Trans. B*, **34B** (2003), 173.
9) R. H. Eric, A. A. Hejja and W. Stange: *Miner. Eng.*, **4** (1991), 1315.
10) E. Jak, H. G. Lee and P. Hayes: *Kor. IMM J.*, **1** (1995), 1.
11) B. Zhao, E. Jak and P. Hayes: *Metall. Mater. Trans. B*, **30B** (1999), 597.
12) E. F. Oshorn, R. C. DeVries, K. H. Gee and H. M. Kraner: *J. Met.*, **6** (1954), 33.
13) G. Cavalier and M. Sandreo-Dendon: *Rev. Metall.*, **57** (1960), 1143.