PHASE EQUILIBRIA IN HIGH MgO FERRO- AND SILICO-MANGANESE SMELTING SLAGS

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ABSTRACT

Phase equilibria have been determined experimentally for pseudo-ternary sections of the form “MnO”-(CaO+MgO)-(SiO_2+Al_2O_3) with a fixed Al_2O_3/SiO_2 weight ratio of 0.17 and MgO/CaO weight ratios of 0.25 and 0.17 respectively for temperatures in the range 1473-1673 K.

The primary phase fields present for the MgO/CaO weight ratio of 0.17 include manganosite (Mn,Mg,Ca)O; dicalcium silicate α-2(Ca,Mg,Mn)O·SiO_2; merwinite 3CaO·(Mg,Mn)O·2SiO_2; wollastonite [(Ca,Mg,Mn)O·SiO_2]; diopside [(CaO,MgO,MnO,Al_2O_3)·SiO_2]; tridymite (SiO_2); tephroite [2(Mn,Mg)O·SiO_2]; rhodonite [(Mn,Mg)O·SiO_2] and melilite [2CaO·(MgO,MnO,Al_2O_3)·2(SiO_2,Al_2O_3)]. For the section with MgO/CaO weight ratio of 0.25 the anorthite phase (CaO·Al_2O_3·2SiO_2) is also present.

The liquidus temperatures of ferro- and silico-manganese smelting slags have been determined. The liquidus temperatures at low MnO concentrations are shown to be principally dependent on the modified basicity weight ratio (CaO+MgO)/(SiO_2+Al_2O_3).

1. INTRODUCTION

The ternary system CaO-“MnO”-SiO_2 [1] has been widely used to describe the general chemical behaviour of ferro- and silico-manganese smelting slags. However, most ores contain significant concentrations of Al_2O_3 and MgO, and the influence of these components cannot be ignored if optimum industrial practice is to be achieved. Al_2O_3 is present in both the ore and the coke ash generated in the reduction process.

In the quaternary system “MnO”-Al_2O_3-CaO-SiO_2 the liquidus temperatures have been determined experimentally at temperatures 1723, 1773 and 1823 K in the primary phase field of manganosite, MnO for Al_2O_3/SiO_2 weight ratios of 0.25 and 0.5 [2]. Liquidus temperatures have also been measured in the system “MnO”-Al_2O_3-CaO-SiO_2 for 6 and 12 wt% MnO sections [3]. The phase equilibria and liquidus isotherms for temperatures between 1473 and 1673 K have been systematically determined in the system “MnO”-Al_2O_3-CaO-SiO_2 for Al_2O_3/SiO_2 weight ratios of 0.41 [4], 0.55 and 0.65 [5]. In these latter studies the results have been presented as pseudo-ternary sections of the quaternary in the form of “MnO”-CaO-(SiO_2+Al_2O_3). This form of representation with “MnO” in one apex provides information that is useful to industrial practice since the changing phase equilibria can be readily followed as manganese is removed from the slag. A number of different sections are required to determine the changing behaviour in silico-manganese production since not only is silicon reduced from the slag but simultaneously SiO_2 and Al_2O_3 components are introduced into the system in the form of coke ash and ore.

MgO is introduced into the smelting process with the ore and cake ash and the concentration in the slag is thus dependent on the source of raw materials. The liquidus temperatures have been measured in the system “MnO”-CaO-MgO-SiO_2-Al_2O_3 at 1723 and 1823 K in the primary phase field of manganosite for Al_2O_3/SiO_2 weight ratio of 0.5 and MgO/CaO weight ratios of 0.5 and 1 [2]. The experiments were focused on a specific composition range and a limited temperature range. The liquidus temperatures of synthetic ferromanganese slags have also been measured by Eric et al [6] using hot-stage microscopy.

Pure oxides were used to prepare the slags in the following composition range: MnO, 5-30 wt%; CaO, 20-35 wt%; MgO, 5-15 wt%; SiO_2, 27-58 wt%; Al_2O_3, 5 wt%; FeO negligible (~0.5 wt%). The experiments were carried out under an argon atmosphere. Ding and Olsen [7] measured some liquidus temperatures in the systems “MnO”-SiO_2, “MnO”-SiO_2-CaO, “MnO”-SiO_2-Al_2O_3 and “MnO”-CaO-SiO_2-Al_2O_3 in equilibrium with Mn-Si-C alloy. No systematic studies of phase equilibria in the system “MnO”-CaO-MgO-SiO_2-Al_2O_3 have been reported.

South African manganese ores and concentrates are characterised by high MgO and low Al_2O_3 contents; the compositions of the slags produced during the production of ferro-alloys from these materials are the focus of the present investigation.

2. EXPERIMENTAL PROCEDURE

The experimental method used in the present study involves high temperature equilibration, quenching and electron probe X-ray microanalysis (EPMA). Details of the experimental procedure have been described in previous publications [8, 9]. During high temperature equilibration the “MnO” and SiO_2 concentrations in the slag change because of vaporisation and reactions with alloy. 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. The experiments are also deliberately targeted so as to provide information on solids and the liquid compositions in local eqilibrium at a known temperature. 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 use in practical application as well as efficient research and further use of experimental information. In the present study of the system “MnO”-CaO-MgO-SiO_2-Al_2O_3 two pseudo-ternary sections have been constructed. The apexes of the pseudo-ternary sections are “MnO”, (CaO+MgO) and (SiO_2+Al_2O_3). The Al_2O_3/SiO_2 weight ratio is fixed at 0.17 and MgO/CaO weight ratios of 0.17 and 0.25 have been selected in the current study. These ratios are close to those in the slags in ferro- 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_2O_3) ratio can be readily examined.

A series of synthetic master slags were prepared from pure MgO, SiO_2, Al_2O_3 and $CaCO_3$ powders (99+%). 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 (99+%) and Mn-Si alloy to obtain final mixtures. The Mn-Si alloy was prepared by mixing Mn (99.9%) and Si (99%) powders with mole ratio of Mn:Si = 3:1 and heating under high purity argon gas in a carbon crucible at 1473 K for 2 hours. Mn-Si alloy 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 experiment was completed.

Approximately 0.3 grams final mixture was pelletised and wrapped into an envelope of Mo foil (0.025mm thick, 99.9+%). Equilibration experiments were carried out in a vertical SiC furnace. The pellet, wrapped in a Mo envelope, was suspended in a Mo dish using a Kanthal wire. The sample was equilibrated at a predetermined temperature for times from 1 to 16 hours depending on the composition and temperature, and then quenched into ice-cooled water.

The quenched samples were mounted and polished for examination. A JEOL 8800L Electron Probe X-ray Microanalyser with Wave Length Dispersion detectors was used for composition analysis. The analysis was conducted at an accelerating voltage of 15 kV and a probe current of 15 nA. The ZAF correction procedure was applied. The average accuracy of the EPMA measurements is within ±1 wt %.

An important feature to note of the systems under investigation is that the compositions of the solid primary phases do not have the same Al_2O_3/SiO_2 and MgO/CaO ratios as the liquid represented in the pseudo-ternary sections. 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 section. The greater the proportion of the solid phase formed, the further the liquid composition is moved away from the 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. Firstly, 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 containing significant volume fraction of melilite to one where only liquid phase is present. The second reason is that all experiments were carried out in the presence of Mn-Si alloy.

A number of reactions always occur including:
$2Mn(metal) + O_2(gas)= 2MnO(slag)$
$Si(metal) + O_2(gas) = SiO_2(slag)$
$Si(metal) + 2MnO(slag) = SiO_2(slag) + 2Mn(metal)$
$Mn(metal) = Mn(gas)$
$Si(metal) + MnO(slag) = SiO(gas) + Mn (metal)$

These reactions change the bulk composition of the oxide melt, which makes it more difficult to control the fraction of solid phases. Although experiments are carefully planned to overcome this problem and to obtain liquid compositions on or near to the selected ratios, in general, this 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. Despite the changes occurring in the bulk compositions of the samples used in these experiments local equilibrium between the liquid and solid phases is achieved, a fact verified in each case by multiple EPMA measurements within the samples.

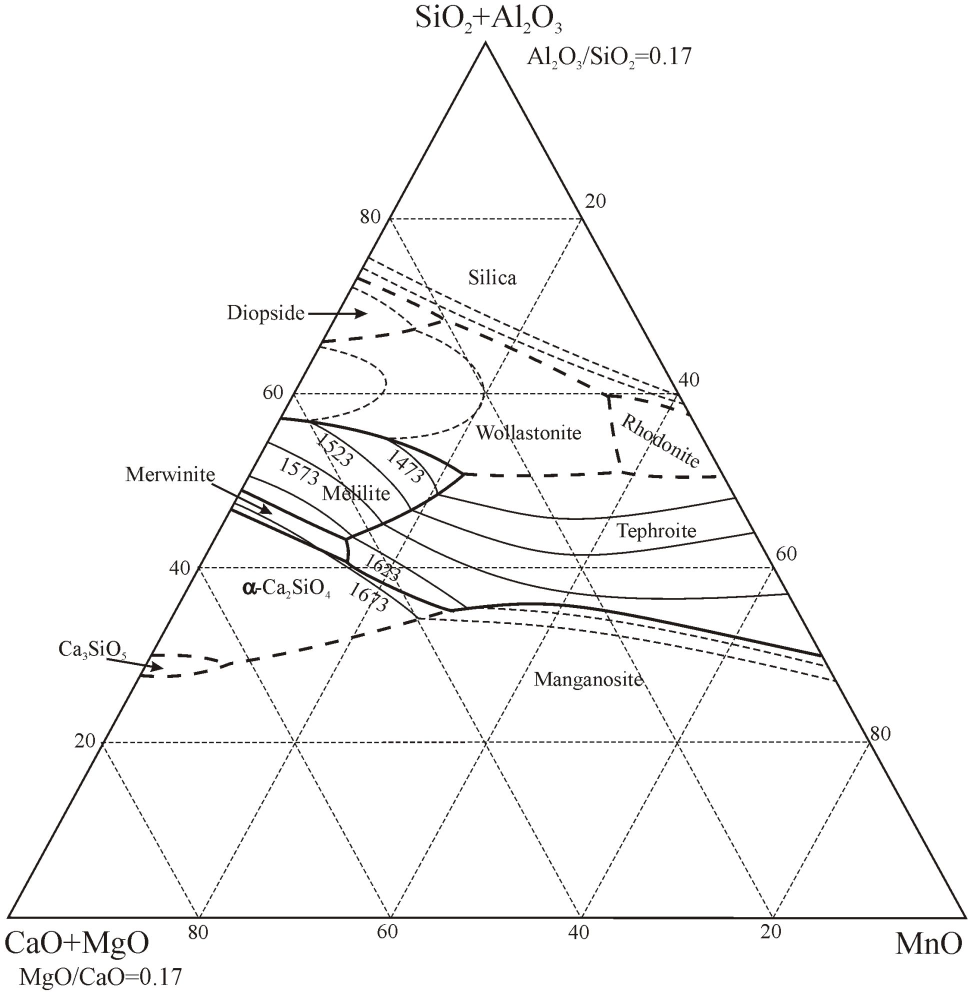

Figure 1. Liquidus of the system "MnO"-CaO-MgO-SiO_2-Al_2O_3 with weight ratios of Al_2O_3/SiO_2=0.17 and MgO/CaO=0.17 in equilibrium with Mn-Si alloy, compositions in wt%, temperatures in K

3. EXPERIMENTAL RESULTS

3.1 Descriptions of the pseudo-ternary sections

The experimental data have been used to construct two sections of the system "MnO"-(CaO+MgO)-(SiO_2+Al_2O_3) with a fixed Al_2O_3/SiO_2 weight ratio of 0.17 and MgO/CaO weight ratios of 0.17 and 0.25 respectively. The pseudo-ternary sections for the five-component system are shown in Figures 1 and 2. The liquidus isotherms at 1473, 1523, 1573, 1623 and 1673 K have been determined.

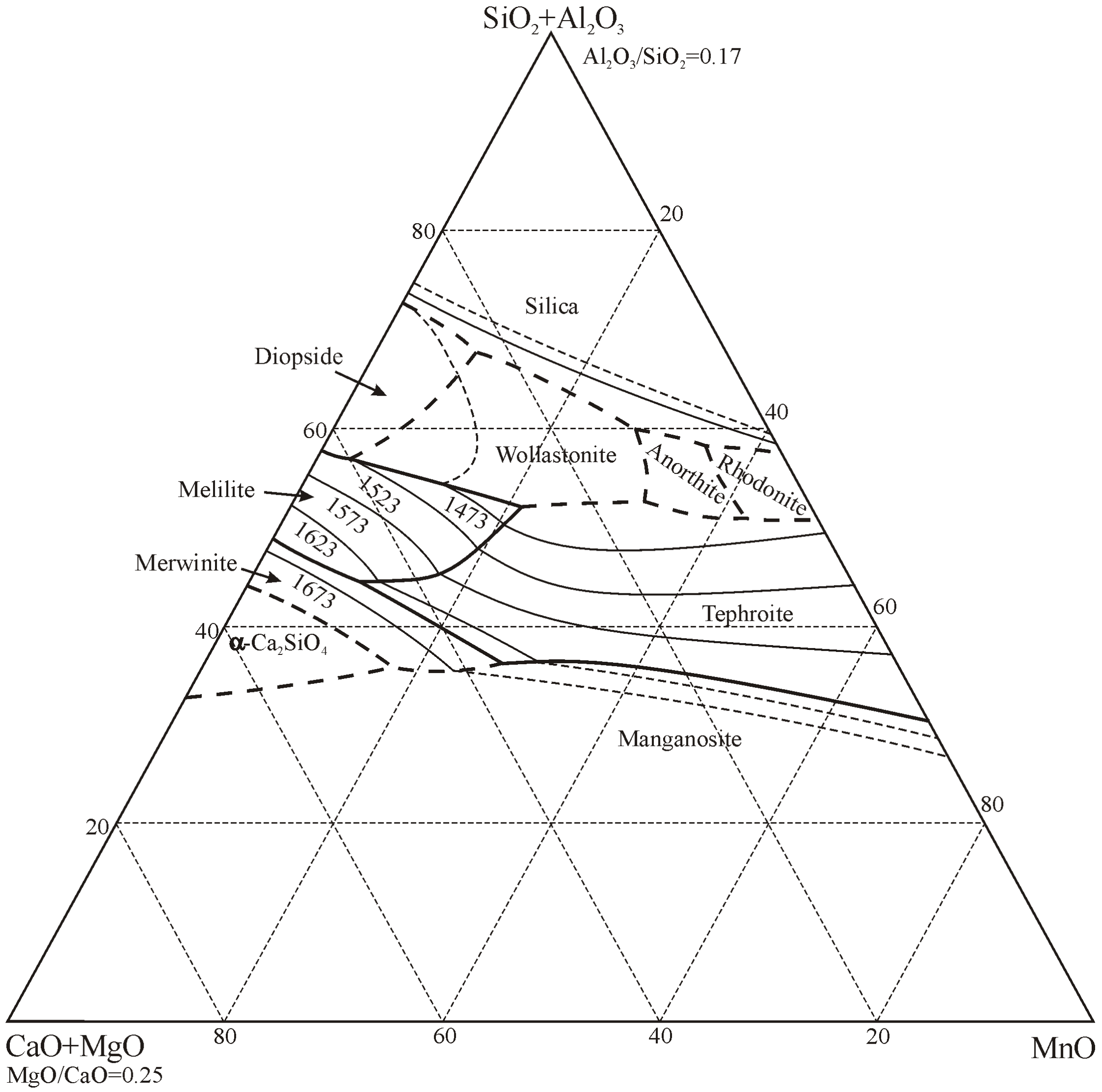

Figure 2. Liquidus of the system "MnO"-CaO-MgO-SiO_2-Al_2O_3 with weight ratios of Al_2O_3/SiO_2=0.17 and MgO/CaO=0.25 in equilibrium with Mn-Si alloy, compositions in wt%, temperatures in K

The phase boundaries marked in Figures 1 and 2 with thick full lines have been accurately determined by experiment; the boundaries marked with dashed lines are approximate. Experimental data were obtained in all primary phase fields including the joins (CaO+MgO)-(SiO_2+Al_2O_3) and "MnO"-(SiO_2+Al_2O_3).

The pseudo-ternary sections are characterised by the presence of the following primary phase fields.

"MnO"-(CaO+MgO)-(SiO_2+Al_2O_3) with Al_2O_3/SiO_2 = 0.17 and MgO/CaO = 0.17

Manganosite (Mn,Mg,Ca)O; dicalcium silicate α-2(Ca,Mg,Mn)O·SiO_2; merwinite 3CaO·(Mg,Mn)O·2SiO_2; wollastonite [(Ca,Mg,Mn)O·SiO_2]; diopside [(CaO,MgO,MnO,Al_2O_3)·SiO_2]; tridymite (SiO_2); tephroite [2(Mn,Mg)O·SiO_2]; rhodonite [(Mn,Mg)O·SiO_2] and melilite [2CaO·(MgO,MnO,Al_2O_3)·2(SiO_2,Al_2O_3)]. The rounded brackets ( ) that appear in some of the above formulae indicate that these compounds can exist over a range of solid solutions, and that the components within the brackets are present in varying proportions depending on the bulk composition of the sample and temperature.

"MnO"-(CaO+MgO)-(SiO_2+Al_2O_3) with $Al_2O_3/SiO_2 = 0.17$ and MgO/CaO = 0.25

This section contains all of the phases mentioned above, and one more phase, anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$).

The experimental results indicate that increasing the MgO/CaO ratio has the effect of increasing the concentration of MgO present in the manganosite phase at any given MnO concentration in the bulk slag, and extending the manganosite primary phase field to lower MnO concentrations.

3.2 Comparison with other systems

The results obtained in the present study in the joins (CaO+MgO)-(SiO_2+Al_2O_3) with fixed Al_2O_3/SiO_2 weight ratio of 0.17 and MgO/CaO weight ratios of 0.17 and 0.25 are in good agreement with those extrapolated from Osborn [10] and Cavalier and Sandreo-Dendon [11].

Comparison of the phase diagram of the system CaO-"MnO"-SiO_2 [1] with the sections determined in the present study of the five component systems containing MgO and Al_2O_3 indicates that whilst the general position of the liquidus valley is similar in the ternary system there are significant differences in the primary phase fields and shape of the liquidus surface.

The rankinite, α'-dicalcium silicate and pseudo-wollastonite primary phase fields in the ternary system CaO-"MnO"-SiO_2 [1] are replaced by melilite, merwinite, diopside and tephroite in the sections of the five component systems. At the same time, most importantly, the liquidus temperatures in the ternary system are significantly different from those in the five-component system.

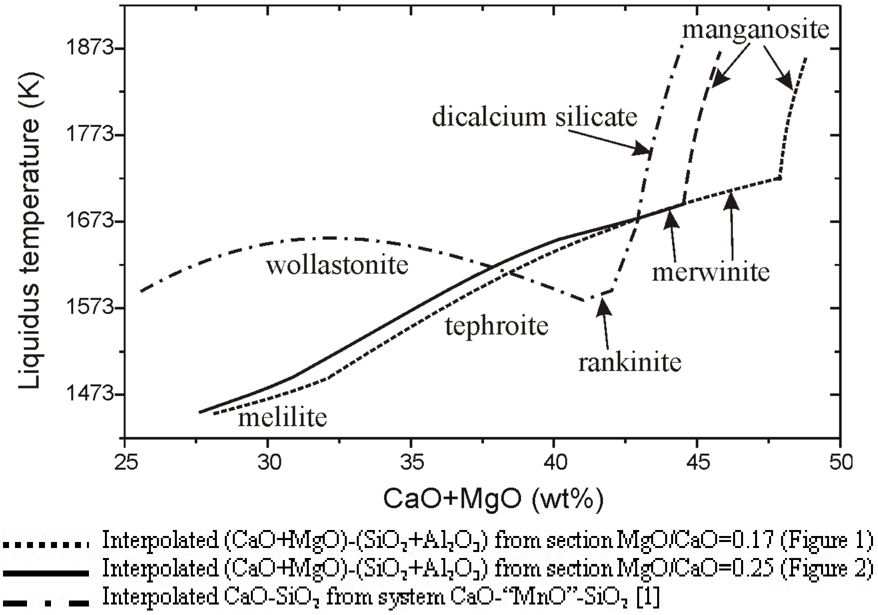

Figure 3. Slag liquidus temperatures for section for 20 wt% MnO.

To assist in the comparison of the liquidus temperatures between the ternary CaO-"MnO"-SiO_2 and the two pseudo-ternary systems "MnO"-(CaO+MgO)-(SiO_2+Al_2O_3) determined in the present study, the liquidus for sections at 20 wt% MnO are presented in Figure 3. It can be seen from Figure 3 that at low (CaO+MgO) concentrations, where the basicity of the liquid is low, 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 in the ternary. In the melilite, merwinite and tephroite primary phase fields the liquidus temperature of the slag gradually increases with increasing (CaO+MgO) concentrations, i.e., basicity. In the manganosite primary phase field the liquidus temperature increases dramatically with increasing basicity of the slag. It can be seen from Figure 3 that at low basicity region, where melilite and tephroite are primary phases, high MgO slags have slightly higher liquidus temperatures. However, at high basicity region, where manganosite is the primary phase, the liquidus temperatures increase significantly with increasing MgO content. This is in good agreement with the trends reported by Eric et al [6]. It was found in the study [6] that at low basicities 0.8 and 1.1 the liquidus temperature slightly decreases with increasing CaO/MgO ratio. In contrast, at higher basicity 1.4 the liquidus temperature significantly decreases with increasing CaO/MgO ratio.

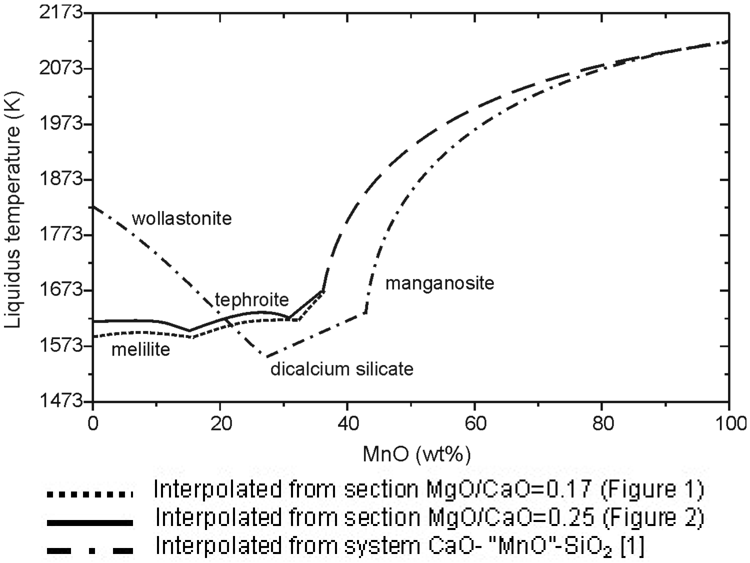

Figure 4. Liquidus temperatures as a function of MnO concentration at a $(CaO+MgO)/(SiO_2+Al_2O_3)$ weight ratio of 0.90

In Figure 4 the change in liquidus temperature with changing MnO concentration is plotted for $(CaO+MgO)/(SiO_2+Al_2O_3)$ ratio of 0.90 to reflect the liquidus as the slags are reduced during the smelting operation. It can be seen that the liquidus profiles for the five component slags with MgO/CaO weight ratios of 0.25 and 0.17 are almost identical to each other. In the region where the MnO concentration is lower than 25 wt% the liquidus temperature in the five component slags does not significantly change with MnO concentration. This behaviour reflects the shape of the liquidus in Figures 1 and 2 where the isotherms in the melilite and tephroite primary phase fields are nearly parallel to the join "MnO"-$[(CaO+MgO)+(SiO_2+Al_2O_3)]$ with $(CaO+MgO)/(SiO_2+Al_2O_3)$ 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.

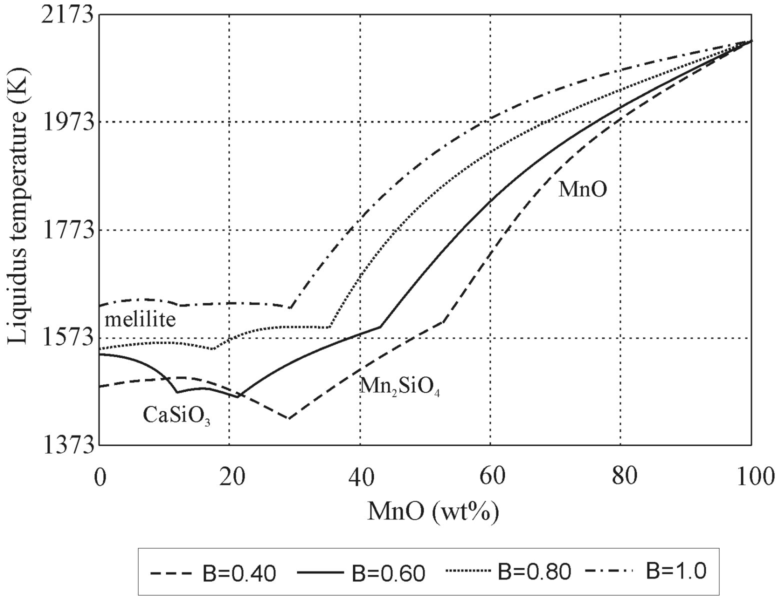

Figure 5.Liquidus temperatures as a function of MnO concentration at various $B=(CaO+MgO)/(SiO_2+Al_2O_3)$ weight ratios interpolated from the five component section with weight ratios of $Al_2O_3/SiO_2=0.17$ and $MgO/CaO=0.17$.

The liquidus temperature as a function of MnO concentration is also compared at various B=(CaO+MgO)/(SiO_2+Al_2O_3) ratios. Figure 5 shows the interpolated results from the multi-component section "MnO"-(CaO+MgO)-(SiO_2+Al_2O_3) with Al_2O_3/SiO_2 weight ratio of 0.17 and MgO/CaO weight ratio of 0.17 (Figure 1). It can be seen from Figure 5 that in high MnO concentration the primary phase is always manganosite (Mn,Mg,Ca)O and the liquidus temperature in this region increases with increasing B. The manganosite primary phase field expands from 46 wt% MnO to 25 wt% MnO when B increases from 0.40 to 1.0. In low MnO concentration the primary phases change with basicity B. When B=0.40 wollastonite [(Ca,Mg,Mn)O·SiO_2] is the primary phase. When B increases to 0.60 wollastonite, melilite [2CaO·(MgO,MnO,Al_2O_3)·2(SiO_2,Al_2O_3)] and tephroite [2(Mn,Mg)O·SiO_2] are the primary phases. At B=0.80 and 1.0 melilite and tephroite are the primary phases. The liquidus temperatures generally increase with increasing B in the same primary phase field.

3.3 The relationship between liquidus temperature and basicity

Eric et al [6] reported a general trend that the liquidus temperatures of manganese smelting slags increase with increasing basicity (CaO+MgO)/SiO_2 at fixed MnO concentrations. From Figures 1 to 3 it can be seen that the liquidus temperatures in the composition range of interest to silico-manganese slags principally depend on the basicity of the slag. The experimental data from present study have been used to determine the relationship between liquidus temperature and basicity of the liquid phase.

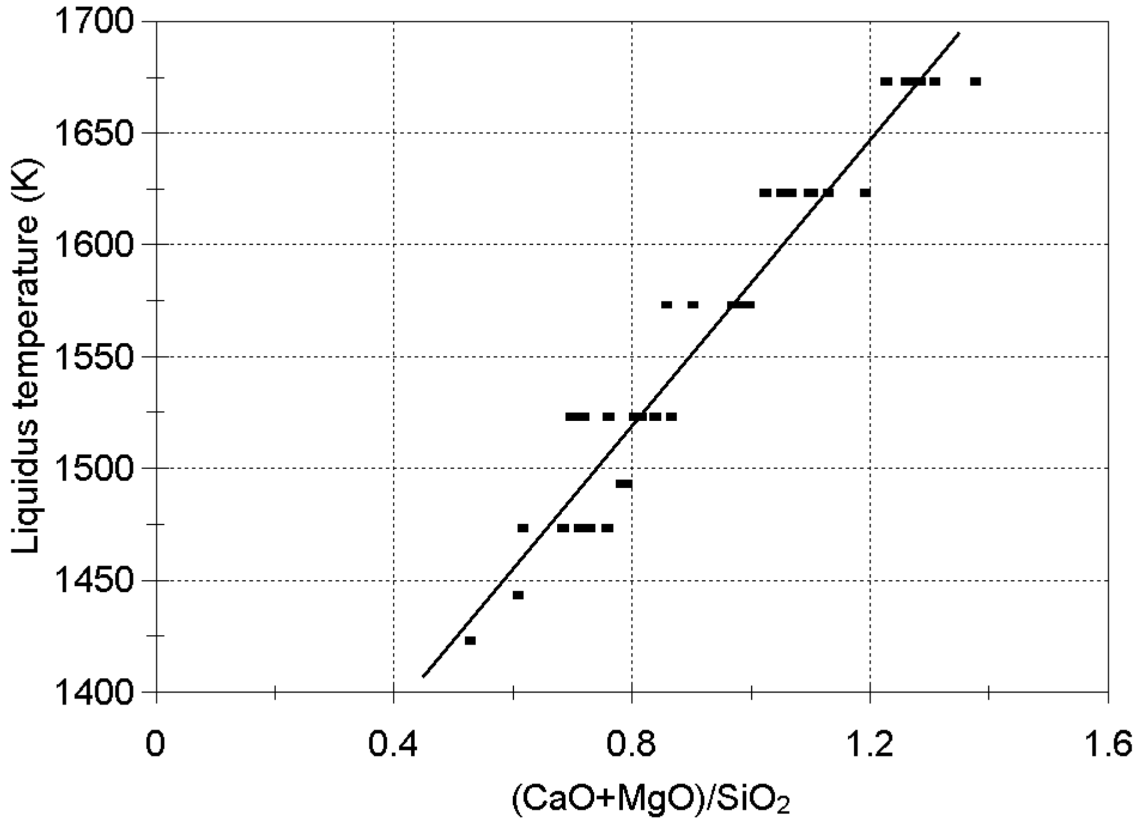

Figure 6. Relationship between liquidus temperatures and traditional basicity of the liquid phase at 10-30 wt% MnO with Al_2O_3/SiO_2 weight ratios of 0.15-0.20 and MgO/CaO weight ratios of 0.15-0.20.

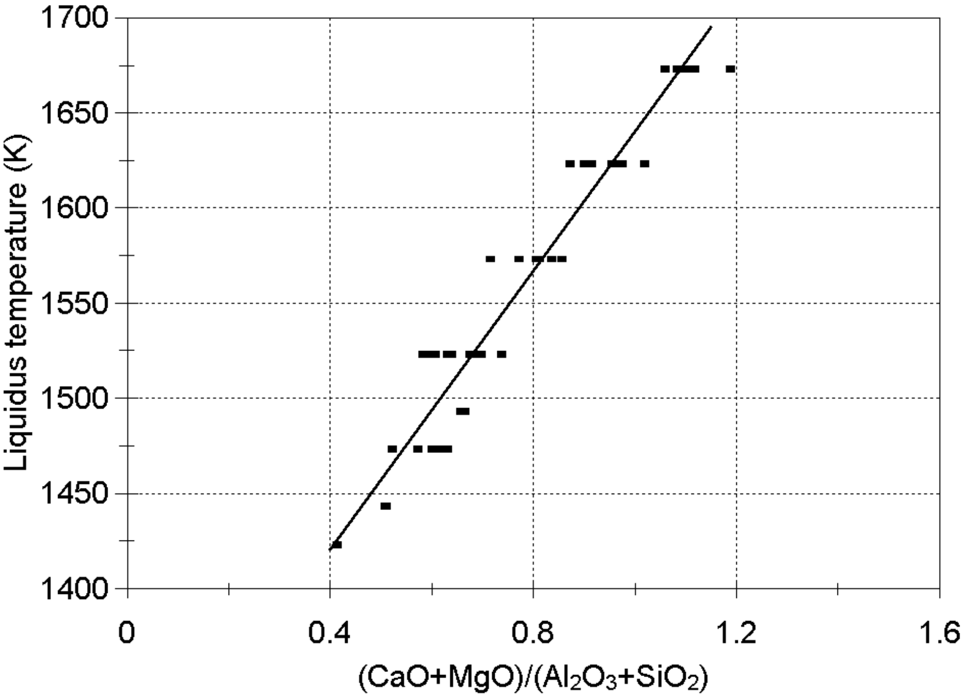

Figure 7. Relationship between liquidus temperatures and modified basicity of the liquid phase at 10-30 wt% MnO with Al_2O_3/SiO_2 weight ratios of 0.15-0.20 and MgO/CaO weight ratios of 0.15-0.20.

Traditionally basicity of these slags are defined in terms of the weight ratio $(CaO+MgO)/SiO_2$. Since in the current study Al_2O_3 is also present in the slags a modified basicity ratio $(CaO+MgO)/(SiO_2+Al_2O_3)$ is introduced. In Figures 6 and 7 the liquidus temperatures are plotted against the traditional and modified basicities for Al_2O_3/SiO_2 ratio 0.15-0.20, MgO/CaO ratio of 0.15-0.20 and MnO concentrations in the range 10-30 wt%. The relationships between liquidus and basicity ratios are approximately linear and are described by the following equations:

$$T_{liq}(K) = 320 \times \frac{(wt\%CaO + wt\%MgO)}{wt\%SiO_2} + 1263 \tag{1}$$

$$T_{liq}(K) = 367 \times \frac{(wt\%CaO + wt\%MgO)}{(wt\%Al_2O_3 + wt\%SiO_2)} + 1273 \tag{2}$$

where: T_{liq} is liquidus temperature in K, $\frac{(wt\%CaO + wt\%MgO)}{wt\%SiO_2}$ is the traditional basicity and

$\frac{(wt\%CaO + wt\%MgO)}{(wt\%Al_2O_3 + wt\%SiO_2)}$ is the modified basicity. Both equations (1) and (2) have correlation coefficients R=0.95.

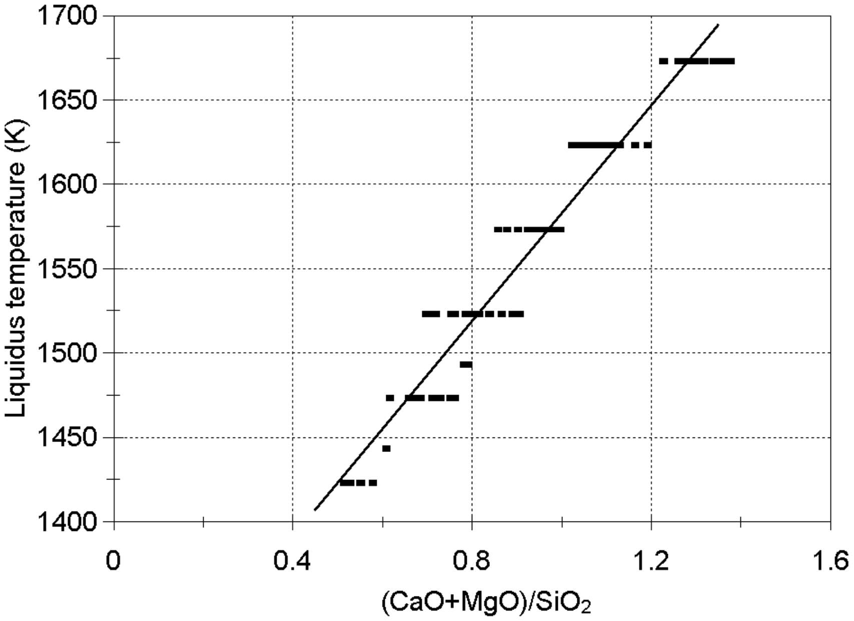

Figure 8. Relationship between liquidus temperatures and traditional basicity of the liquid phase at 10-30 wt% MnO with Al_2O_3/SiO_2 weight ratios of 0.13-0.27 and MgO/CaO weight ratios of 0.09-0.29

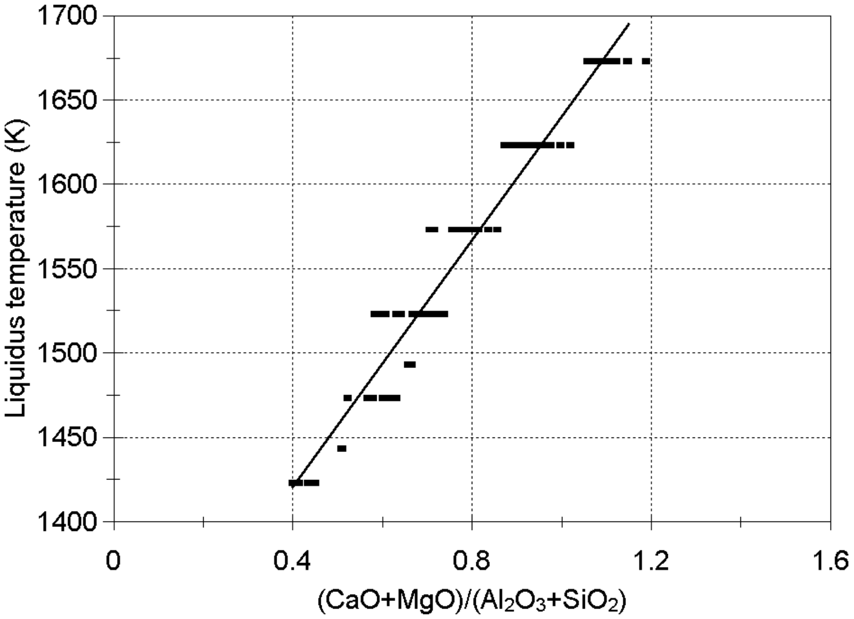

Figure 9. Relationship between liquidus temperatures and modified basicity of the liquid phase at 10-30 wt% MnO with Al_2O_3/SiO_2 weight ratios of 0.13-0.27 and MgO/CaO weight ratios of 0.09-0.29

The same equations have been used to describe the liquidus data over a range of compositions from Al_2O_3/SiO_2 ratio 0.13-0.27, MgO/CaO ratio of 0.09-0.29 and MnO concentrations in the range 10-30 wt% (see Figures 8 and 9). The experimental data used in these correlations are in the melilite, merwinite and tephroite primary phase fields. The empirical correlations are not necessarily valid outside of the range of compositions reported here.

4. CONCLUSIONS

The liquidus temperatures and phase relations in the system “MnO”-(CaO+MgO)-(SiO_2+Al_2O_3) with a fixed Al_2O_3/SiO_2 weight ratio of 0.17 and MgO/CaO weight ratios of 0.25 and 0.17 respectively under argon in equilibrium with Mn-Si alloy have been determined.

The phases present at the liquidus surfaces in this system for a MgO/CaO weight ratio of 0.17 include: manganosite (Mn,Mg,Ca)O; dicalcium silicate α-2(Ca,Mg,Mn)O·SiO_2; merwinite 3CaO·(Mg,Mn)O·2SiO_2; wollastonite [(Ca,Mg,Mn)O·SiO_2]; diopside [(CaO,MgO,MnO,Al_2O_3)·SiO_2]; tridymite (SiO_2); tephroite [2(Mn,Mg)O·SiO_2]; rhodonite [(Mn,Mg)O·SiO_2] and melilite [2CaO·(MgO,MnO,Al_2O_3)·2(SiO_2,Al_2O_3)]. For the section with MgO/CaO weight ratio of 0.25 the anorthite phase (CaO·Al_2O_3·2SiO_2) is also present.

The liquidus temperatures and primary phase fields are markedly different from the system CaO-MnO-SiO_2 under reducing conditions. The liquidus temperature at low MnO concentrations is shown to be principally dependent on the modified basicity weight ratio (CaO+MgO)/(SiO_2+Al_2O_3).

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