



PHASE EQUILIBRIA IN K_2O -CONTAINING MANGANESE SMELTING SLAGS

B. Zhao, S. Ganguly¹, E. Jak and P. Hayes

PYROSEARCH, Pyrometallurgy Research Centre, School of Engineering
The University of Queensland, Brisbane, Queensland, Australia

¹Tasmanian Electrometallurgical Company TEMCO, BHP Billiton

Georgetown, Tasmania, Australia

E-mail: B.Zhao@minmet.uq.edu.au;

ABSTRACT

Slag samples taken from adjacent to the furnace wall of a submerged arc ferromanganese smelting furnace have been found to contain high concentrations of K_2O . To characterize the phase equilibria relevant to these slags experimental studies have been carried out to determine pseudo-ternary sections of the form " MnO "- CaO -($SiO_2+Al_2O_3$) with a fixed Al_2O_3/SiO_2 weight ratio of 0.65 and 6.0 wt% K_2O for temperatures in the range 1523-1673 K.

In the pseudo-ternary section investigated the primary phase fields are found to be mullite, $3Al_2O_3 \cdot 2SiO_2$; corundum, Al_2O_3 ; spinel, $MnO \cdot Al_2O_3$; manganosite solid solution, $(Mn,Ca)O$; dicalcium silicate, $2CaO \cdot SiO_2$; gehlenite $2CaO \cdot Al_2O_3 \cdot SiO_2$; anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$; kalsilite $KAlSiO_4$ and leucite $KAlSi_2O_6$.

It was found that the presence of K_2O in the slag decreases liquidus temperature in the anorthite and gehlenite primary phase fields. The manganosite primary phase field is expanded in the direction of increased ($Al_2O_3+SiO_2$) and the liquidus temperatures in the manganosite primary phase field are increased significantly with the presence of K_2O in the slag.

1. INTRODUCTION

Excavation of submerged arc ferromanganese smelting furnaces [1-2] have shown that a number of different zones exist in the furnace during operation. These zones are characterized by differences in temperature, and differences in the phases present and their compositions. Whereas immediately below the electrode tip there is an active high temperature "coke bed" consisting of a dispersion of coke, slag and alloy, adjacent to the furnace walls there are banks of immobile sintered charge. Analyses of the slags [2] present in the furnace shows that the concentration of K_2O in the coke bed is low, and that high concentrations of K_2O are present in the charge above the hot zone and in the cooler banks of material near the furnace walls. These observations indicate that significant movement of alkalis takes place through the gas phase with vaporization.

Manganese ores from Australia contain up to 1.8 wt% K_2O [3] and it is therefore expected that high alkali slags would be found in furnaces using these ores.

MnO , CaO , SiO_2 and Al_2O_3 are the major components of ferro- and silico-manganese slags. The phase equilibria in the system " MnO "- Al_2O_3 - CaO - SiO_2 [4-5] have been investigated in previous studies by PYROSEARCH. However, there are no data available at present on the liquidus temperatures of potassium enriched slags found adjacent to the furnace wall.

2. EXPERIMENTAL

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 that described in previous publication [6]. During high temperature equilibration the K_2O , " MnO " and SiO_2 concentrations in the

slag change because of vaporisation and reactions with Mn-Si alloy present in the system. However, with the present experimental methodology these changes do not affect the final results since the measurements of the phase compositions are carried out after 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-SiO₂-Al₂O₃-K₂O, a pseudo-ternary section has been constructed as shown in Figure 1. The apices of the pseudo-ternary section are “MnO”, CaO and (SiO₂+Al₂O₃) all having 6 wt% K₂O. The Al₂O₃/SiO₂ weight ratio is fixed at 0.65 and K₂O concentration in the liquid is 6.0 wt%. This Al₂O₃/SiO₂ ratio has been selected since it is close to that in the ferro-manganese slags of smelters using manganese ores from Groote Eylandt, Australia.

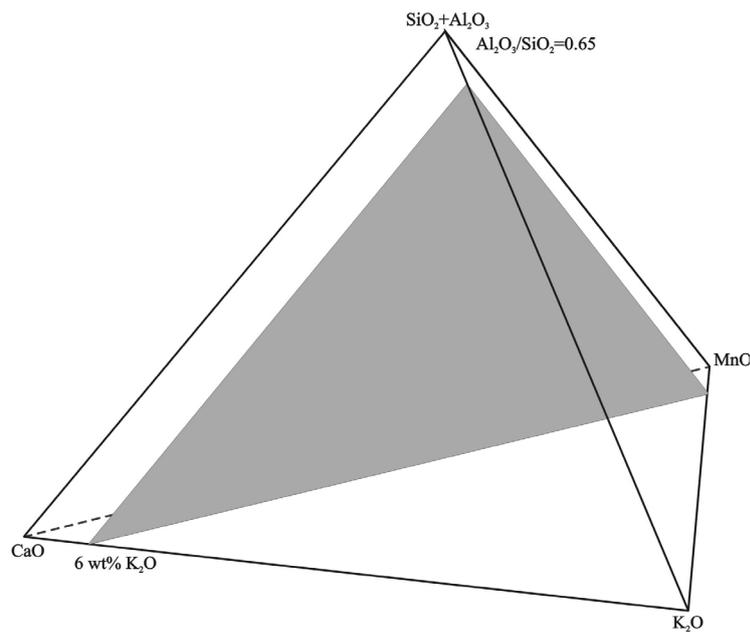


Figure 1: Pseudo-ternary sections “MnO”-(CaO+MgO)-(SiO₂+Al₂O₃) with Al₂O₃/SiO₂ weight ratio of 0.65 and 6 wt% K₂O in equilibrium with Mn-Si alloy

A series of synthetic master slags were prepared from high purity (99+%) SiO₂, Al₂O₃, KHCO₃ and CaCO₃ powders at high temperature so that

- (i) all starting mixtures have the same Al₂O₃/SiO₂ ratio and K₂O content,
- (ii) the components of the sample are well mixed ensuring that equilibrium can be easily achieved,
- (iii) the K₂O is incorporated into the slag to reduce the vaporisation of potassium at high temperatures.

In order to minimise foaming of the melt and K₂O vaporisation, K₂O-SiO₂ glass was first prepared following the procedure described by Roedder [7], and Schairer and Bowen [8]. In brief, 10.0 g KHCO₃ and 6.0 g SiO₂ were mixed in an agate mortar and pressed into 10mm diameter tablets. The tablets were placed in a platinum crucible covered with a lid. The mixture and crucible were heated in a muffle furnace for 24 hours at 973 K. Then the temperature of the furnace was raised to 1173 K and kept at this temperature for 1 hour and then 1273 K for 24 hours. Finally the temperature of the furnace was raised to 1573 K and kept at this temperature for 2 hour and the sample was cooled rapidly to room temperature and placed in a desiccator.

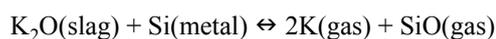
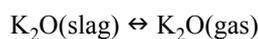
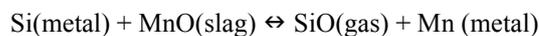
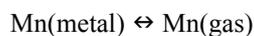
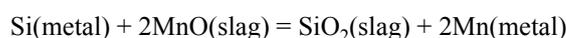
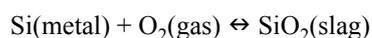
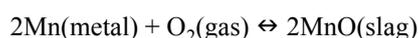
To prepare the master slags to be used in the equilibration experiments, K₂O-SiO₂ glass, SiO₂, Al₂O₃ and CaCO₃ powders were mixed in an agate mortar with desired proportions. The pelletised mixtures were then placed in a platinum crucible and heated in air at 1873 K for several hours. The quenched master slags were

ground and mixed with MnO and Mn-Si alloy to obtain the final mixtures. The Mn-Si alloy was prepared by mixing Mn and Si powders with mole ratio of Mn:Si = 3:1 and treated in a carbon crucible at 1473 K for 2 hours under Ar atmosphere. The alloy was crushed and milled to $\approx 100\mu\text{m}$. Mn-Si alloy was added to the slag to ensure that the manganese is present in its lowest oxidation state Mn^{2+} . Sufficient alloy powder was added to ensure that alloy is still dispersed throughout the sample after equilibration is complete.

Approximately 0.3 grams 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 lanthanum chromite elements (PYROX, France). The mixture, wrapped in a Mo envelope, was suspended in a Mo dish using a Kanthal wire. The samples were equilibrated at a predetermined temperature for times from 1 to 16 hours depending on their compositions and temperatures, and then quenched into ice-cooled water.

The quenched samples were mounted and polished for metallographic examination. A JEOL 8800L Electron Probe X-ray Microanalyser (EPMA) with Wave Length Dispersive detectors was used for measurements of the phase compositions. The standards used for EPMA include alumina (Al_2O_3) for Al, spessartine ($\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) for Mn, orthoclase (KAlSi_3O_8) for K 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+} .

An important feature to note of the systems under investigation is that the compositions of the solid primary phases do not have the same $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio and K_2O concentration as those indicated in the pseudo-ternary section. The precipitation of these crystals from the melt will result in the selective removal of the components from the liquid phase into the solid phase. 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 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 K_2O and Mn-Si alloy. A number of reactions may occur including:



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 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 section 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 with a fact verified in each case by multiple EPMA measurements within the samples.

3. RESULTS

3.1 Bulk Chemical Analysis of the Dig-out Samples

Two slag samples provided by TEMCO were analysed by Inductively Coupled Plasma (ICP). One sample was taken from directly against the carbon of the furnace lining (wall slag) and the other one was 20 cm away from the carbon (called bulk slag). The compositions of the wall slag and bulk slag determined by ICP are given in Table 1.

Table 1: Bulk compositions of the industrial ferromanganese slag samples determined by ICP (wt%)

	Ca	Mn	Al	Si	K	Na	Mg	Fe	Ba	Cr	Ti	V
Bulk slag	2.65	49.44	1.71	3.36	3.2	0.45	0.58	8.44	0.57	0.02	0.1	0.02
Wall slag	2.66	48.25	4.39	1.84	5.33	0.62	1.33	4.55	0.59	0.02	0.11	0.02

EPMA analyses of these samples show that all Fe and some of Mn are present in form of Fe-Mn alloy. Other components are present in the slag as oxides. It can be seen from Table 1 that CaO, MnO, Al_2O_3 , SiO_2 and K_2O are the major components of the oxide slag. The potassium concentration is higher in the wall slag than that in bulk slag.

3.2 Quenching Experiments Using Industrial Slag

Reheating and quenching experiments have been carried out in argon gas using the wall slag and bulk slag with the compositions given in Table 1. The slag samples were ground to powder, then pelletised and wrapped in a Mo envelope. The experiments were carried out in the temperature range 1373 to 1673 K. After equilibration the sample was quenched in cool water. The compositions of the phases present in the quenched samples were analysed by EPMA. It was found that

1. All samples were in equilibrium with Mn-Fe alloy although the composition of the alloy varies in different samples;
2. The manganosite is the only primary phase for wall slag above 1623 K and for bulk slag above 1573 K which indicates that both the wall slag and the bulk slag are located in manganosite primary phase field;
3. At lower temperatures spinel $[(Mn,Mg)O \cdot Al_2O_3]$, kalsilite ($KAlSiO_4$) and dicalcium silicate ($2CaO \cdot SiO_2$) are observed in the slag samples;
4. In the samples where manganosite is the only solid phase the Al_2O_3/SiO_2 ratio in liquid represents its value in the bulk composition, that is 0.87 for wall slag and 0.62 for bulk slag;
5. $KAlSiO_4$ phase disappears at temperatures above between 1473 and 1573 K releasing K_2O into the liquid phase.
6. Substantial K_2O losses from the slag at temperatures above 1573 K.

3.3 Experiments Using Synthetic Slag

The pseudo-ternary section " MnO "-CaO-($SiO_2+Al_2O_3$) with Al_2O_3/SiO_2 weight ratio of 0.65 has been investigated previously [5]. For a purpose of comparison the liquidus surfaces of the pseudo-ternary section of " MnO "-CaO-($Al_2O_3+SiO_2$) with Al_2O_3/SiO_2 weight ratio of 0.65 are presented in Figure 2.

In the pseudo-ternary section of " MnO "-CaO-($Al_2O_3+SiO_2$) with Al_2O_3/SiO_2 weight ratio of 0.65 [5] the primary phase fields include mullite, $3Al_2O_3 \cdot 2SiO_2$; corundum, Al_2O_3 ; spinel, $MnO \cdot Al_2O_3$; manganosite sol-

id solution, (Mn,Ca)O; dicalcium silicate, $2\text{CaO}\cdot\text{SiO}_2$; gehlenite $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, and anorthite $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$.

A pseudo-ternary section “MnO”-CaO-($\text{SiO}_2+\text{Al}_2\text{O}_3$) with $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratio of 0.65 and 6.0 wt% K_2O is selected in the present study to enable the effect of K_2O on the phase equilibria to be analysed. The experimentally determined liquidus surfaces for this section are presented in Figures 3 and 4. Figure 3 shows the liquidus data points obtained in the present investigation. The pseudo-ternary section shown in Figures 3 and 4 illustrates the absolute concentrations of MnO, CaO and ($\text{SiO}_2+\text{Al}_2\text{O}_3$) in the liquid phase. Only the liquid compositions having close $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratio of 0.65 and 6.0 wt% K_2O are used in the construction of the pseudo-ternary section.

It can be seen from Figure 4 that the pseudo-ternary section “MnO”-CaO-($\text{Al}_2\text{O}_3+\text{SiO}_2$) with $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratio of 0.65 and 6 wt% K_2O , contains all primary phase fields present in the system without K_2O [5], i.e., mullite, $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$; corundum, Al_2O_3 ; spinel, $\text{MnO}\cdot\text{Al}_2\text{O}_3$; manganosite solid solution, (Mn,Ca)O; dicalcium silicate, $2\text{CaO}\cdot\text{SiO}_2$; gehlenite $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, and anorthite $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$. In addition, two new primary phase fields of kalsilite KAlSiO_4 and leucite KAlSi_2O_6 are introduced as a result of K_2O addition. The liquidus isotherms in this section have been determined between 1523 and 1673 K at 50 degrees intervals.

The primary phase fields for KAlSiO_4 and KAlSi_2O_6 in this section appear between the primary phase fields of gehlenite $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$, anorthite $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and galaxite (spinel) $\text{MnO}\cdot\text{Al}_2\text{O}_3$, and result in a general increase in liquidus temperatures in this region compared to the K_2O -free system [5]. In particular it is noted that the low temperature region present at the join between the gehlenite and anorthite primary phase fields in the K_2O -free system in the range of 0-30% “MnO” is almost eliminated on introduction of the K_2O .

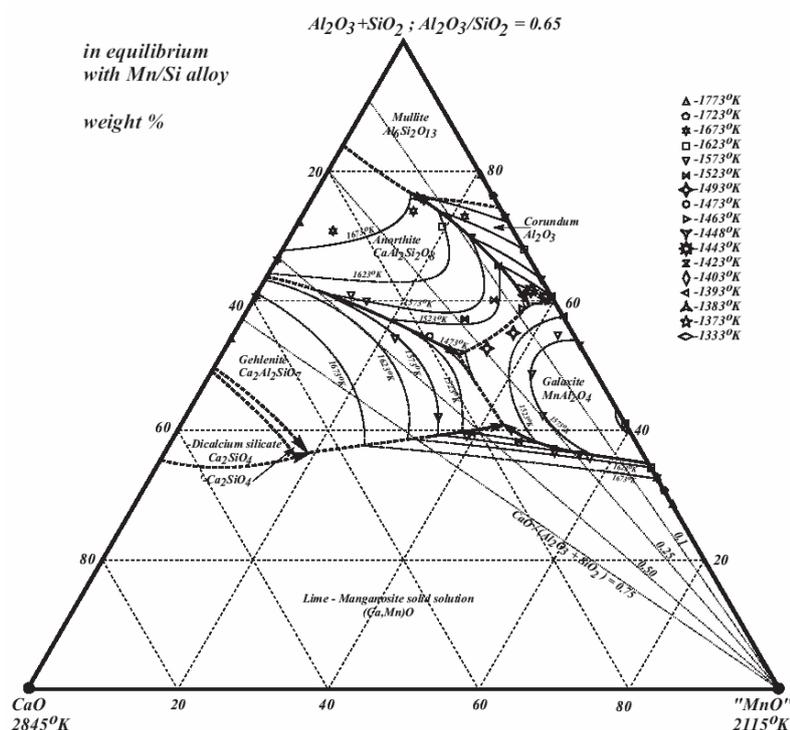


Figure 2: Experimentally determined liquidus isotherms in the “MnO”-CaO-($\text{Al}_2\text{O}_3+\text{SiO}_2$) system with $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratio of 0.65 in equilibrium with Mn-Si alloy [5]

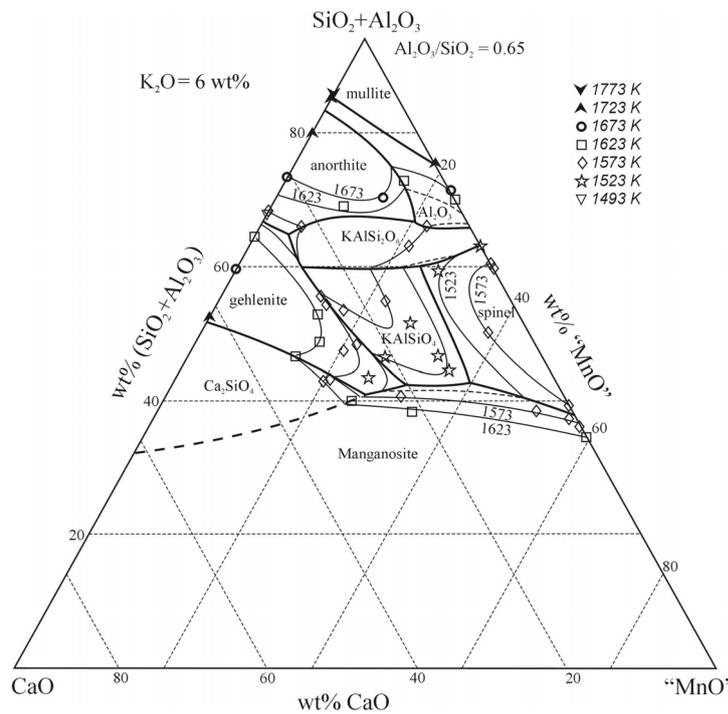


Figure 3: Experimentally determined liquidus isotherms in the “MnO”-CaO-($Al_2O_3+SiO_2$)- K_2O system with Al_2O_3/SiO_2 weight ratio of 0.65 and 6 wt% K_2O in equilibrium with Mn-Si alloy

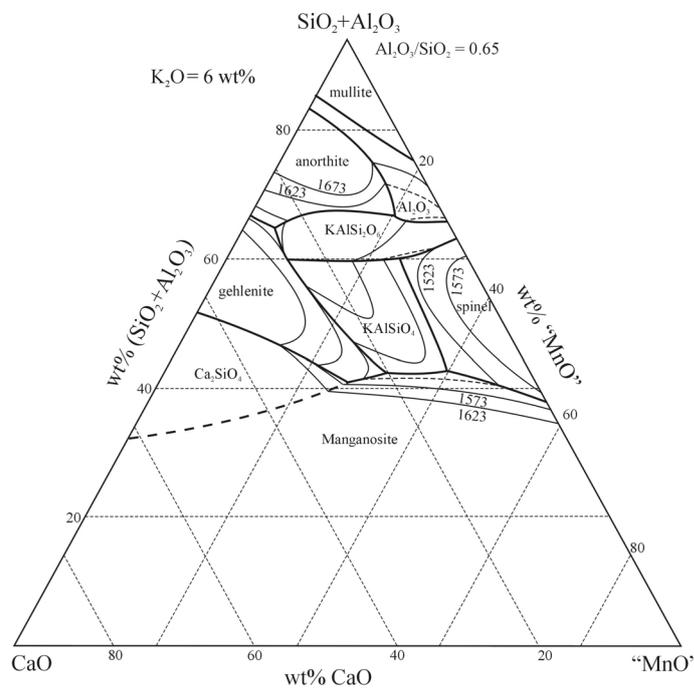


Figure 4: Experimentally determined liquidus isotherms in the “MnO”-CaO-($Al_2O_3+SiO_2$)- K_2O system with Al_2O_3/SiO_2 weight ratio of 0.65 and 6 wt% K_2O in equilibrium with Mn-Si alloy

Examples of typical microstructures in the present study observed using backscattered electron imaging are presented in Figures 5 to 7. Figure 5 illustrates the microstructure of the manganosite (MnO) in equilibrium with liquid and Mn-Si alloy. The coexistence of spinel ($\text{MnO}\cdot\text{Al}_2\text{O}_3$) and kalsilite (KAlSiO_4) in equilibrium with liquid and Mn-Si alloy is shown in Figure 6. Figure 7 shows the coexistence of dicalcium silicate ($2\text{CaO}\cdot\text{SiO}_2$) and gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) in equilibrium with liquid and Mn-Si alloy.

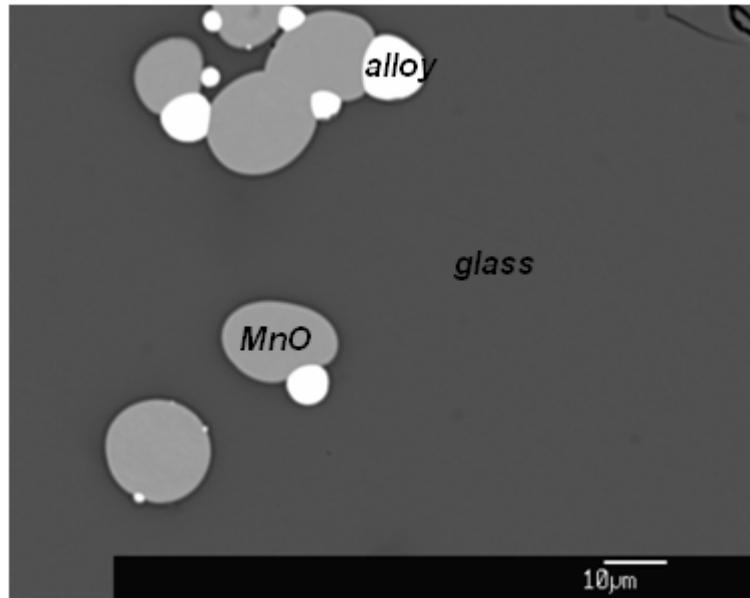


Figure 5: Backscattered electron image of manganosite (MnO) in equilibrium with liquid and Mn-Si alloy

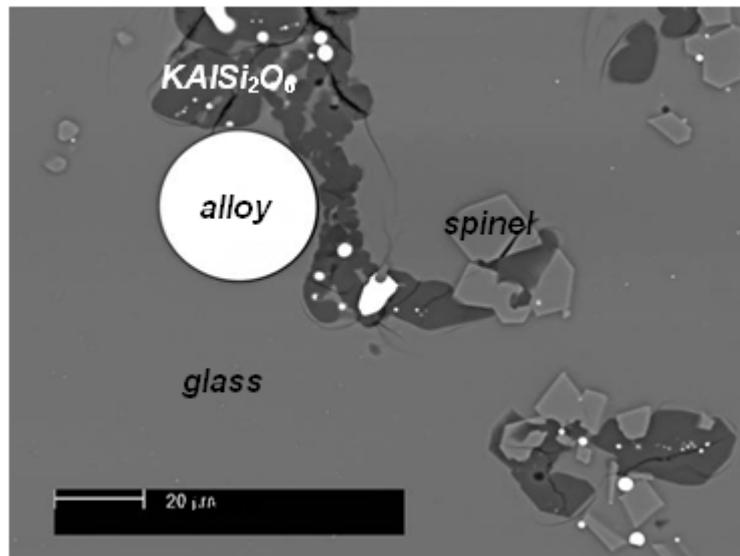


Figure 6: Backscattered electron image showing the coexistence of spinel ($\text{MnO}\cdot\text{Al}_2\text{O}_3$) and kalsilite (KAlSiO_4) in equilibrium with liquid and Mn-Si alloy

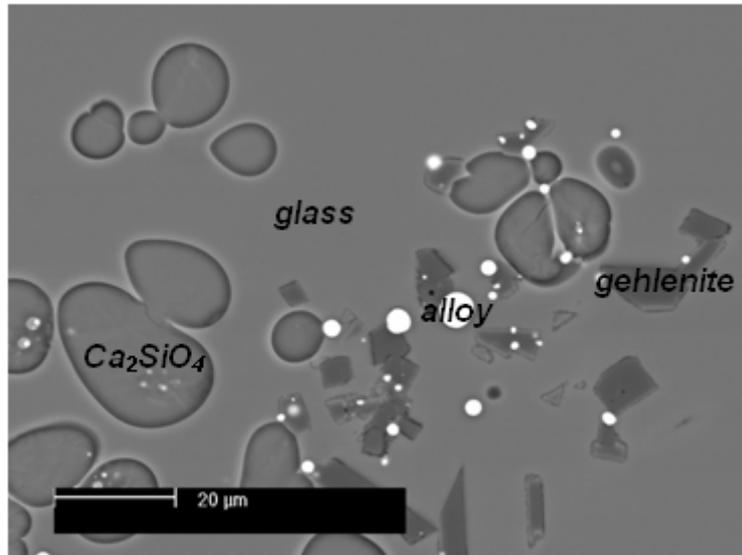


Figure 7: Backscattered electron image showing the coexistence of dicalcium silicate ($2CaO \cdot SiO_2$) and gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) in equilibrium with liquid and Mn-Si alloy

A pseudo-binary section “MnO”-($CaO+Al_2O_3+SiO_2$) with $Al_2O_3/SiO_2=0.65$ and $CaO/(Al_2O_3+SiO_2)=0.42$ is constructed using the present results and previous results [5] to compare the effect of K_2O addition on liquidus temperature (Figure 8). In the K_2O -free system this section passes through anorthite, gehlenite and manganosite primary phase fields. With the addition of 6 wt% K_2O the gehlenite primary phase field is replaced by leucite and kalsilite primary phase fields. It can be seen from Figure 8 that in the silicates primary phase fields addition of K_2O generally decreases the liquidus temperature. However, the manganosite phase is stabilised and the liquidus temperature in the manganosite primary phase field is significantly increased with the addition of K_2O . It can be seen that with addition of 6 wt% K_2O the manganosite phase is formed at 34 wt% “MnO” comparing to that formed at 42 wt% “MnO” without K_2O addition. The liquidus temperature in the manganosite primary phase field is increased by approximately 150 degrees Centigrade with addition of 6 wt% K_2O .

As mentioned in Section 3.2 that compositions of the TEMCO ferromanganese smelting slags are located in the manganosite primary phase field. Accumulation of K_2O inside the furnace increases its concentration in the slag, which results in the increase of the liquidus temperature of the slag. These K_2O -rich slags stay inside the furnace as accretion. Formation of excessive accretion may have a serious influence on the furnace performance and refractory wear. The solubility of K_2O in the slag is important information to remove the K_2O from the furnace. It has been reported [9] that in iron blast furnace slag the concentration of K_2O increases with decreasing basicity of the slag, i.e., $(CaO+MgO)/SiO_2$. In the present study the similar results are observed. It can be seen from Figure 9 that at fixed temperature the K_2O content in ferromanganese slag increases with decreasing modified basicity $(CaO+MnO)/(SiO_2+Al_2O_3)$. For example, at 1400 °C the concentration of K_2O in the slag is increased from 3.5 to 10 wt% as the modified basicity is decreased from 1.6 to 1.2.

The compositions of the alloy are also important for ferro- and silico-manganese smelting. In the present study it was found that Si content in Mn-Si alloy increases with increasing $(SiO_2+Al_2O_3)$ concentrations in the liquid phase as shown in Figure 10.

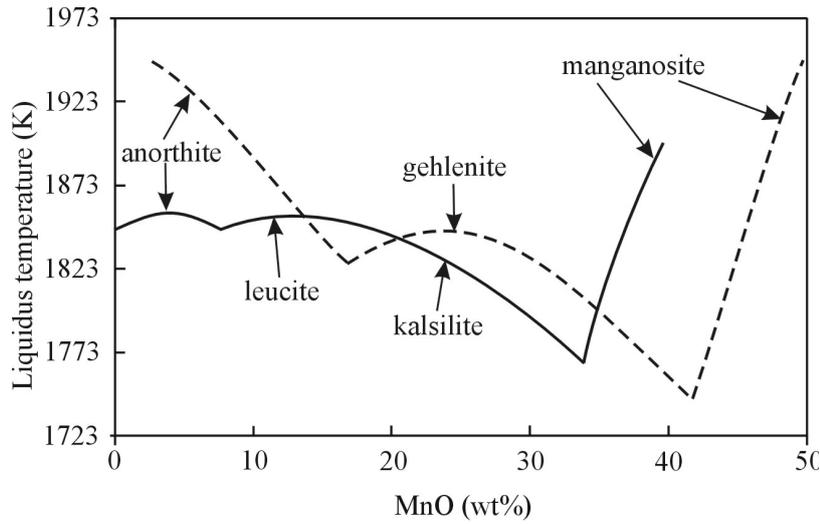


Figure 8: Comparison of liquidus temperatures for the slags with and without K_2O in the join “MnO”- $(CaO+Al_2O_3+SiO_2)$ with $Al_2O_3/SiO_2=0.65$ and $CaO/(Al_2O_3+SiO_2)=0.42$
 Dashed line: without K_2O [5]; Solid line: 6 wt% K_2O , present work

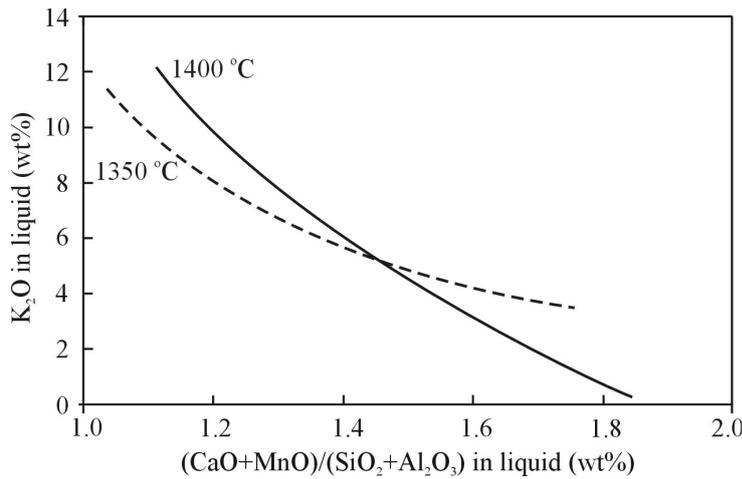


Figure 9: Relationship between $(CaO+MnO)/(Al_2O_3+SiO_2)$ in liquid and K_2O in liquid in ferromanganese slag samples quenched from 1673 K in the manganosite primary phase field

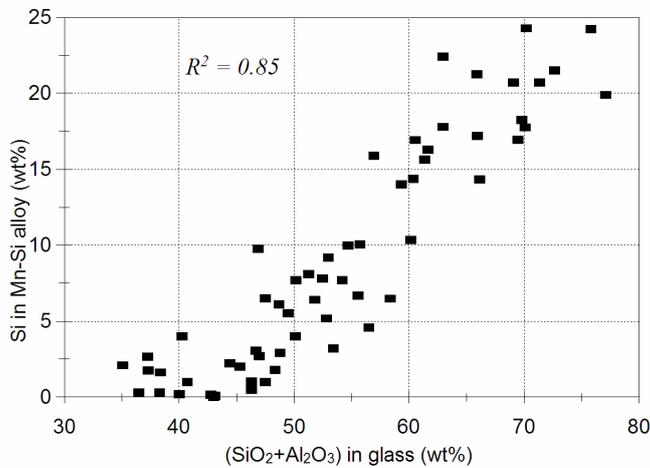


Figure 10: Apparent relationship between $(SiO_2+Al_2O_3)$ concentrations in liquid and Si content in Mn-Si alloy in temperature range of 1473 to 1723 K

4. INDUSTRIAL IMPLICATIONS

Previous phase equilibrium studies of SiO_2 - K_2O [11] and SiO_2 - Al_2O_3 - K_2O [8] systems have shown the presence of K_2O can dramatically decrease the liquidus temperatures in certain composition ranges. It can be seen from the ternary system SiO_2 - Al_2O_3 - K_2O (see Figure 11) that compared to low Al_2O_3 slags the formation of $KAlSi_2O_6$ and $KAlSiO_4$ is favored by increasing Al_2O_3/SiO_2 ratio in the liquid slag.

The phase equilibrium studies for “MnO”- CaO - SiO_2 - Al_2O_3 - K_2O system for $Al_2O_3/SiO_2 = 0.65$ and 6 wt% K_2O carried out in the present study have shown that in the presence of up to 6 wt% K_2O does not markedly decrease the liquidus temperatures in the composition range of interest to ferromanganese smelting, i.e. at or close to MnO saturation. In fact the low melting temperature region of the “MnO”- CaO - SiO_2 - Al_2O_3 system between the galaxite, gehlenite and anorthite primary phase fields (Figure 2) have been replaced by primary phase fields of $KAlSi_2O_6$ and $KAlSiO_4$. The present findings are consistent with those of the SiO_2 - Al_2O_3 - K_2O ternary with the formation of the stable potassium aluminosilicate phases.

The effect of K_2O is to slightly lower the liquidus in the gehlenite and anorthite primary phase fields relative to the potassium-free system; this may be significant in the case of silico-manganese smelting.

The findings in the present study are relevant to the design of refractory of freeze linings, since as indicated in the opening remarks, redistribution of potassium through the vapor phase does occur in submerged arc ferromanganese and silico-manganese smelting furnaces. In general the stability of freeze lining and reduced refractory attack is favored by increased slag liquidus temperatures. Although the Groote Eylandt ores are higher in K_2O than many manganese ores, they also contain higher Al_2O_3/SiO_2 ratios; it would appear that in

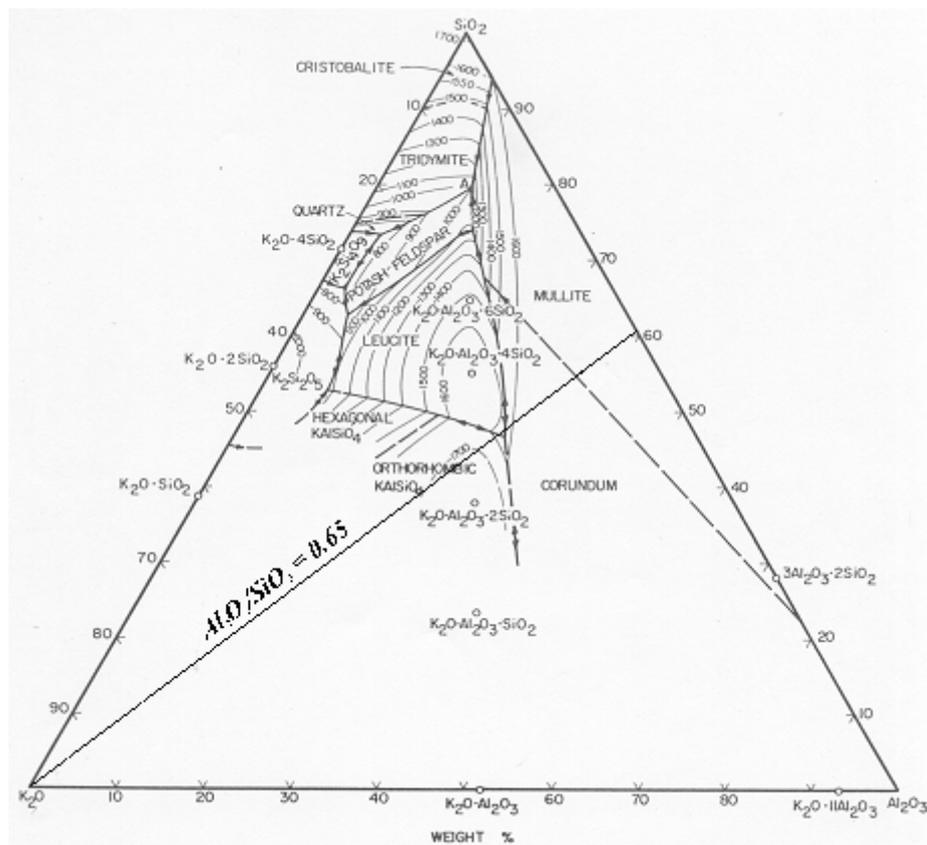


Figure 11 :Phase diagram for the system K_2O - Al_2O_3 - SiO_2 in air[10]

this case the combination of both K_2O and Al_2O_3 in the feed is generally advantageous in maintaining high slag liquidus temperatures.

5. CONCLUSIONS

Experiments have been carried out in the system “MnO”- Al_2O_3 -CaO- SiO_2 - K_2O in equilibrium with Mn-Si alloy. The liquidus isotherms in the temperature range of 1523-1773 K have been determined for the pseudo-ternary section CaO-“MnO”-($Al_2O_3+SiO_2$) with Al_2O_3/SiO_2 weight ratio of 0.65 and 6.0 wt% K_2O . In this pseudo-ternary section the primary phase fields are found to be mullite, $3Al_2O_3 \cdot 2SiO_2$; corundum, Al_2O_3 ; spinel, $MnO \cdot Al_2O_3$; manganosite solid solution, (Mn,Ca)O; dicalcium silicate, $2CaO \cdot SiO_2$; gehlenite $2CaO \cdot Al_2O_3 \cdot SiO_2$, anorthite $CaO \cdot Al_2O_3 \cdot 2SiO_2$, kalsilite $KAlSiO_4$ and leucite $KAlSi_2O_6$.

It was found that addition of K_2O in the slag decreases liquidus temperature in the anorthite and gehlenite primary phase fields, the manganosite primary phase field is expanded towards ($Al_2O_3+SiO_2$) direction, and the liquidus temperatures in the manganosite primary phase field are increased significantly with increasing K_2O concentration.

It was found that solubility of K_2O in ferromanganese slag increases with decreasing modified basicity $(CaO+MnO)/(Al_2O_3+SiO_2)$. Si content in Mn-Si alloy was found to increase with increasing ($SiO_2+Al_2O_3$) concentrations in the liquid phase at fixed temperature.

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