High Temperature Phase and Thermodynamic Relations in Selected MnO-CrO_x Systems

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ABSTRACT

Phase- and thermodynamic relations in MnO-CrO_x-containing systems were examined in order to establish a knowledge base for the substitution of nickel in stainless steels by manganese. Phase relations were determined in the pseudo-binary and ternary systems which constitute the (MnO-CrO_x-CaO-SiO_2) system, under steelmaking conditions (i.e. high temperatures and highly reducing conditions). The most prominent characteristic common to these MnO-CrO_x-containing systems, is the dominance of the $(Mn,Cr)_3O_4$ spinel phase and the small all-liquid phase fields. MnO activity-composition relations were determined in (MnO-CrO_x-CaO-SiO_2) - containing melts, which were saturated with the $(Mn,Cr)_3O_4$ spinel phase, using the gas-slag-platinum equilibration technique. By using the experimentally determined values for $\ln\gamma_{Mn}$ in Pt-Cr-Mn alloys, the MnO activities and MnO activity coefficients were calculated. It was found that an increase in the concentration of MnO in the melt increases both the MnO activity and the MnO activity coefficient. In addition, it was discovered that for a constant MnO concentration in the melt, the activity of MnO (and therefore the activity coefficient of MnO) is increased by an increase in the basicity of the melt.

1. INTRODUCTION

Since South Africa is blessed with large reserves of chromium and manganese, but only limited amounts of nickel, it is of great importance that the potential of the production of high-manganese austenitic stainless steels on a large scale in South Africa be investigated. Of major concern to potential high-manganese stainless steels producers however, is a high loss of manganese through volatilization, due to high manganese partial pressures under steelmaking conditions. It is therefore of fundamental and great practical importance to determine to what extent the recovery of both manganese and chromium, but specifically manganese, in the smelting and subsequent refining processes of these stainless steels can be optimized. Theoretical considerations indicate that high manganese losses can be minimized by keeping the steelmaking temperature as low as possible, and by the use of slags with high MnO activities at low concentrations of MnO in the slag.

The incentive for this study arose from the fact that knowledge of phase- and thermodynamic relations in oxide systems that contain both CrO_x and MnO is very limited. Such information is a necessary prerequisite for the study of reactions between slag components, the evaluation and prediction of slag-refractory interactions, as well as to acquire a better understanding of the precipitation of certain oxide inclusions in stainless steels during solidification.

The work presented in this paper can be divided into two main objectives: The first objective centres on the determination of phase relations, under steelmaking conditions, in pseudo-binary and ternary systems which constitute the pseudo-quaternary (MnO-CrO_x-CaO-SiO_2) system. The second objective focuses on the determination of MnO activity-composition relations in (MnO-CrO_x-CaO-SiO_2)-containing melts at 1500°C (2732°F) and an oxygen partial pressure of $10^{-8.99}$ atm.

2. EXPERIMENTAL

A vertical Alsint alumina (99.7% Al_2O_3) tube furnace which is heated by six U-shaped Super Kanthal 33 (molybdenum disilicide) heating elements was used in the equilibration experiments. The oxygen partial pressure (PO_2) in the furnace was controlled by mixing high purity CO (99.9%) and CO_2 (99.995%) according to the tables of Deines *et al.* (1). Oxygen in the CO was removed by passing it through a tube furnace which contained chromium powder and titanium filings at 900°C. CO_2 in the CO was removed by passing the CO through ascarite (NaOH on asbestos), while the water was removed by anhydrone ($Mg(ClO_4)$), drierite ($CaSO_4$) and KOH. The purified CO was then mixed with the CO_2 gas by passing it through Messer Griesheim Oxisorb and Hydrosorb gas purification columns. These columns removed trace amounts of oxygen and water from the gas. The flow of each gas component was controlled by means of a needle valve and measured with a Fischer and Porter snap-in variable area flowmeter. The flow meters were calibrated by using the soap bubble technique. This gas mixture was introduced into the work tube through the gas inlet at the bottom of the furnace at a linear flow rate of 0.9cm/s (0.35"/s), in order to minimize thermal diffusion (2). The oxygen partial pressure in the furnace at specific gas ratios and temperatures was assessed by the Fe-'FeO' equilibrium (3). It was determined that the oxygen potentials in the present study is correct to within $\pm 0.05 \log_{10}$ units.

Samples were quenched in either an ice-water slurry or liquid nitrogen (in the case of samples which contained a hydratable CaO-rich phase). The sample was dropped into the quenching medium by passing a current through molybdenum wire leads of the sample holder, from which the samples were suspended by a thin molybdenum wire (Figure 1). When the thin molybdenum wire melted, the sample dropped into the quench-bath through a plastic foil, by which the bottom end of the furnace tube was sealed.

The temperature inside the furnace was measured with a type-B (Pt-6%Rh - Pt-30%Rh) work thermocouple, which was calibrated on a regular basis against a type-B calibration thermocouple. The calibration thermocouple in turn, was calibrated against the melting points of gold and palladium (respectively 1064.43°C (1947.97°F) and 1554°C (2829°F) (4)). The temperature profile in the furnace yielded a hot zone, 4cm (1.57") in length, in which the temperature varied by less than ±1°C.

Analytical grade Cr_2O_3 (99.999%), CaO (99.95%) and SiO_2 (99.99%) were dried at 1200°C (2192°F) for 24 hours, before use. Bright green MnO was produced by the conversion of analytical grade $MnCO_3$ (99.95%) at 1200°C (2192°F) in air to Mn_3O_4, followed by crushing and reaction in a platinum-lined alumina crucible at 1100°C (2012°F) in a stream of pure hydrogen gas for 3 hours. The masses of the oxides were determined to an accuracy of 0.1 mg in the desired proportions and intimately mixed by wet grinding in a McCrone Micronising Mill. The mixtures were then air dried, pelletised and pre-reacted in platinum crucibles at 1200°C (2192°F) for 24 hours under atmospheres sufficiency reducing to keep manganese in the divalent state (Mn^{2+}).

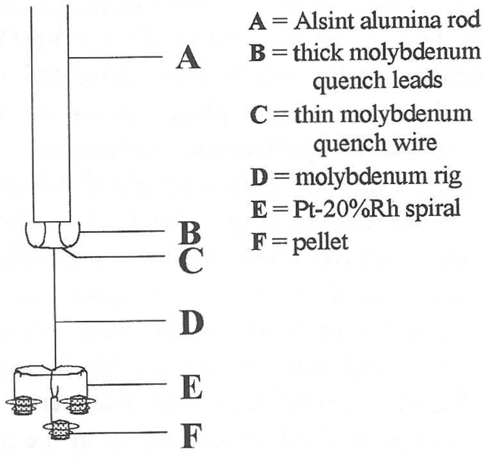

Fig. 1. Assembly by which the samples were suspended in the hot zone.

2.1 Sample preparation procedure used in the study of phase relations

The time required to reach equilibrium was determined by the reaction of samples in the pseudo-binary Cr_2O_3-MnO system to be 14 hours at 1400°C (2552°F). The pre-reacted samples were subsequently reacted at the desired temperature and oxygen partial pressure for 24 hours. Samples with a mass of 0.5-1.0 g were contained in either platinum foil crucibles, platinum or Pt-20%Rh spirals, and were suspended from a molybdenum rig as shown in Figure 1. Spiral sample holders were developed to contain samples which contained a large fraction of liquid phases because the semi-liquid slags crept out of the platinum foil crucibles which were originally used as containers. The spirals easily contained the green pellets, while on reaction, the surface tension between the liquid slag phase and the spiral was sufficient to maintain the samples in position, and no creep was detected. By using the design shown in Figure 1 it was possible to react and quench three samples simultaneously.

The crystalline phases were analyzed by using a scanning electron microscope (SEM), employing energy dispersive spectrometry (EDS), while the glass phases were analyzed by electron microprobe analysis (EMPA), using wavelength dispersive spectrometry (WDS). A Jeol JSM-840A scanning microscope was used for the EDS analysis, using a single standard semi-quantitative analysis technique. The WDS analysis was performed on an ARL-SEMQ electron microprobe. Phase identification in the MnO-CrO_x-containing systems was further supplemented by X-ray powder diffraction (XRD) and reflected light microscopy. A Siemens D500 diffractometer, using Cu-Kα radiation, was used for the XRD analyses.

2.2 Sample preparation procedure used in the study of MnO activities

When samples were prepared for MnO activity determinations, pre-reacted mixtures were re-pelletised together with platinum coils, whereby oxide pellets with entrained pieces of platinum, were formed. The coils were made from platinum wire, 0.3mm in diameter and of 99.95% purity. In these experiments it was found that 48 hours were sufficient to reach equilibrium. The slag samples were subsequently equilibrated with the entrained platinum wire at 1500°C (2732°F) and an oxygen partial pressure of $10^{-8.99}$ atm., by suspending the samples in platinum spirals, as shown in Figure 1.

The resultant Pt-Mn-Cr alloy coils were broken out of the quenched slag sample, and analyzed by performing area analyses (50µm x 60µm) on the Jeol JSM-840A scanning electron microscope (SEM), using energy dispersive spectrometry (EDS). The liquid phases of the analogous slag samples were analyzed on an ARL-SEMQ electron microprobe, using wavelength dispersive spectrometry (WDS) analysis.

3. RESULTS

3.1 Phase relations

3.1.1 The MnO-CrO_x system

Phase relations in the MnO-Cr_2O_3 system were examined under intermediate reducing conditions in order to limit the loss of MnO through the reaction $MnO(s) \Leftrightarrow Mn(g) + 1/2O_2(g)$. An atmosphere with a CO/CO_2 volume ratio of 4.8 (the CO/CO_2 ratio which fixes the oxygen partial pressure of the Fe-FeO buffer at 1600°C (2912°F) (5)) was chosen to produce these intermediate reducing conditions. The resulting oxygen potential of $Po_2=10^{-9}$ at 1500°C (2732°F) is slightly higher than that conventionally used in the study of oxide systems under steelmaking conditions. The MnO losses from the samples were such that the MnO content of the various phases varied by less than 1% MnO by mass throughout the sample. Phase relations were therefore studied under steady-state rather than equilibrium conditions, but for the purposes of this study it was assumed that phase relations under steady-state conditions reflect equilibrium phase relations.

Phase relations in the $MnO-Cr_2O_3$ system are shown in Figure 2. The system is not truly binary because both chromium and manganese can exist in the 2+ and 3+ oxidation states under the experimental conditions pertaining to this study. However, for the sake of simplicity the phase relations are projected onto the binary $MnO-Cr_2O_3$ diagram.

In Figure 2 phase fields are shown in which the solid solution (Mn,Cr)O, [(Mn,Cr)O + spinel], spinel and [spinel + Cr_2O_3] are the stable phases respectively. The spinel phase may consequently be regarded as the dominant compound in the $MnO-Cr_2O_3$ system under reducing conditions. The stoichiometries of the spinels in the spinel stability field can range from $Mn_1^{2+}Mn_y^{3+}Cr_{2-y}^{3+}O_4$ to $Mn_{1-x}^{2+}Cr_x^{2+}Cr_2^{3+}O_4$, which includes the stoichiometric spinel $MnCr_2O_4$. An increase in temperature increases the concentration of Cr^{2+} in both the (Mn,Cr)O phase and the $(Mn,Cr)_3O_4$ spinel phase, as well as the size of the spinel stability field.

The concentration of Cr^{2+} in the spinel phase can also be increased by lowering the oxygen partial pressure at a specific temperature. Figure 3 indicates that the stoichiometries of the spinels in the [spinel+Cr_2O_3] phase field can range from $Mn_{0.91}^{2+}Cr_{0.03}^{2+}Cr_{2.04}^{3+}O_4$ to $Mn_{0.69}^{2+}Cr_{0.09}^{2+}Cr_{2.14}^{3+}O_4$ as the oxygen partial pressure is decreased from $10^{-8.99}$ to $10^{-12.00}$ atm.

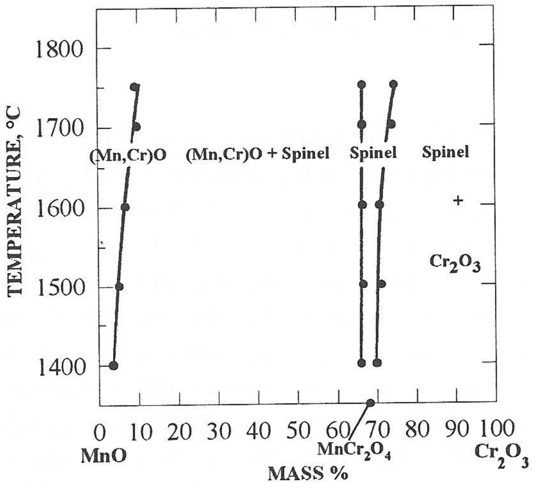

Fig. 2. Phase equilibria in the $MnO-Cr_2O_3$ system, in an atmosphere with a CO/CO_2 volume ratio of 4.8.

3.1.2 The CrO_x-CaO-MnO system

The 1500°C (2732°F) isotherm of the pseudo-ternary Cr_2O_3-CaO-MnO system under an oxygen partial pressure of $10^{-8.99}$ atm. is shown in Figure 4. Characteristic of this 1500°C (2732°F) isotherm, is the fact that phase relations are all sub-solidus, and that the system is dominated by the presence of the $(Mn,Cr)_3O_4$ spinel and orthorhombic β-$CaCr_2O_4$. Phase fields in which (Mn,Ca,Cr)O, [$(Mn,Cr)_3O_4$ + (Mn,Ca,Cr)O], [β-$CaCr_2O_4$ + (Mn,Ca,Cr)O + $(Mn,Cr)_3O_4$], [β-$CaCr_2O_4$ + (Mn,Ca,Cr)O], [β-$CaCr_2O_4$ + $(Mn,Cr)_3O_4$] and [β-$CaCr_2O_4$+$(Mn,Cr)_3O_4$+Cr_2O_3] are the stable phases, can be distinguished. Although it is known that a complete solid solution series exists between CaO and MnO (6), it was not found to be the case for the ternary system CrO_x-CaO-MnO. The amount of CrO in the metal oxide structure decreases from 4.7 to 0 mass% CrO as the amount of CaO increases from 0 to 100 % CaO by mass. Limited solid solution of CaO in the spinel phase, and of MnO in the calcium chromite phase, were observed. A maximum of 3.0 mass% CaO can be accommodated in the $(Mn,Cr)_3O_4$ spinel structure, while up to 3.2 mass% MnO can dissolve in the β-$CaCr_2O_4$ under the present experimental conditions.

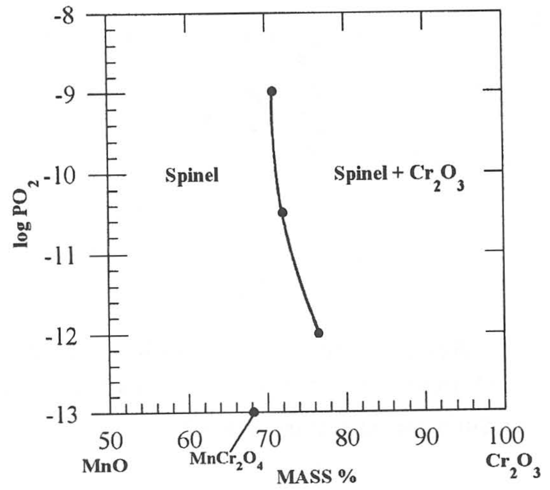

Fig. 3. The position of the spinel-[spinel + Cr_2O_3] phase boundary as a function of oxygen partial pressure (atm.) at 1500°C (2732°F).

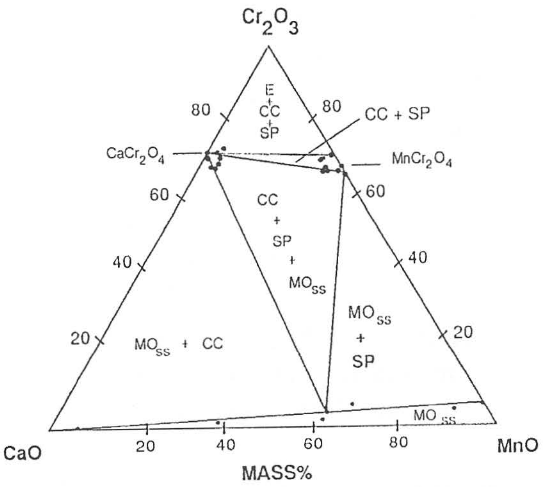

Fig. 4. The pseudo-ternary Cr_2O_3-CaO-MnO system at 1500°C (2732°F) and oxygen partial pressure of $10^{-8.99}$ atm. (E = Cr_2O_3, CC = β-$CaCr_2O_4$, SP = $(Mn,Cr)_3O_4$, MO_{ss} = $(Mn,Ca,Cr)O$)

3.1.3 The Cr_2O_3-SiO_2-MnO system

The 1500°C (2732°F) isotherm of the Cr_2O_3-SiO_2-MnO system under an oxygen partial pressure of $10^{-8.99}$ atm. is shown in Figure 5. It was found that in this system phase fields exist in which [Cr_2O_3+ cristobalite + $(Mn,Cr)_3O_4$], [$(Mn,Cr)_3O_4$ + cristobalite + liquid], [liquid+ cristobalite], liquid, [liquid+ $(Mn,Cr)_3O_4$], [$(Mn,Cr)_3O_4$+liquid+$(Mn,Cr)O$] and [liquid +$(Mn,Cr)O$] are the stable phases. Characteristic of this isotherm is, again, the dominance of the $(Mn,Cr)_3O_4$ spinel phase. A maximum of 4.5 % Cr_2O_3 by mass can be dissolved in the liquid phase before this spinel phase precipitates under the present experimental conditions. An increase in the SiO_2 content of the liquid phase results in a small increase in the solubility of the $(Mn,Cr)_3O_4$ spinel until cristobalite precipitates from the melt. Spinels with a Cr_2O_3 content which exceeds that of stoichiometric $MnCr_2O_4$, contain chromium in both the 2+ and 3+ oxidation states.

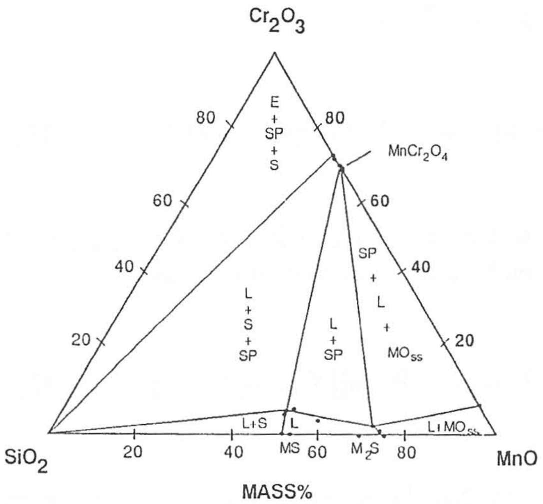

Fig. 5. The pseudo-ternary Cr_2O_3-SiO_2-MnO system at 1500°C (2732°F) and oxygen partial pressure of $10^{-8.99}$ atm. (E = Cr_2O_3, SP = $(Mn,Cr)_3O_4$, S= cristobalite, L=liquid, MO_{ss}=$(Mn,Cr)O$ MS = $MnSiO_3$, M$_2$S = Mn_2SiO_4)

3.2 Activity-composition relations of MnO in $MnO-CrO_x-CaO-SiO_2$-containing slags

MnO activities in ($MnO-CrO_x-CaO-SiO_2$)-containing melts, which were saturated with the $(Mn,Cr)_3O_4$ spinel phase, were determined at 1500°C (2732°F) and under an oxygen partial pressure of $10^{-8.99}$ atm. This was done by equilibrating the samples with platinum, whereby the following equilibrium was established:

$$[Mn]_{platinum} + 1/2O_2(g) \Leftrightarrow MnO(\ell) \qquad [1]$$

The activity of MnO in the melt (a_{MnO}) could then be calculated from the equation:

$$RT\ln a_{MnO} = RT\ln[(X_{Mn} \cdot \gamma_{Mn})P_{O_2}^{0.5}] - \Delta G_1^{o} \qquad [2]$$

where X_{Mn} is the mole fraction of manganese in the platinum (which was determined by EDS analysis), γ_{Mn} is the activity coefficient of manganese in the resultant Pt-Cr-Mn alloy, PO_2 is the imposed oxygen partial pressure of $10^{-8.99}$ atm., and ΔG_1^{o} is the standard free energy of equation [1]. Darken's quadratic formalism for binary and ternary metallic solutions were used to calculate the activity coefficient of manganese in the Pt-Cr-Mn system, in which platinum was considered to be the solvent (7).

The calculated activities of MnO (a_{MnO}) in the ($MnO-CrO_x-CaO-SiO_2$)-containing melts are shown in Figure 6 as a function of MnO concentration (X_{MnO}). The activity coefficients of MnO (γ_{MnO}) in ($MnO-CrO_x-CaO-SiO_2$)-containing melts of equal MnO concentration, are shown as a function of basicity in Figure 7. It follows that an increase in the concentration of MnO in the melt, increases the MnO activity. It was also found, similar to the behaviour of MnO in ferromanganese slags, that the concentration of MnO influences its own activity coefficient. In the MnO concentration range under investigation ($0 \leq X_{MnO} \leq 0.34$) the activity coefficient of MnO increases as the concentration increases. At constant MnO concentration in the melt, the activity of MnO, and therefore the activity coefficient of MnO, can be increased by increasing the basicity of the melt. A pronounced effect is achieved when the basicity of the slag is increased from 0.2 to 1.0. In order to improve the recovery

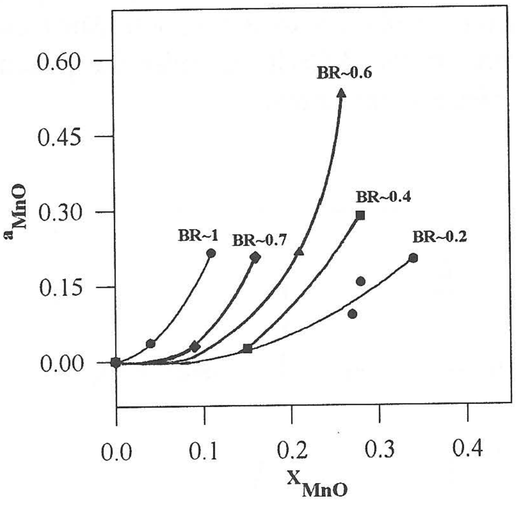

Fig. 6. Activity-composition relations of MnO in ($MnO-CrO_x-CaO-SiO_2$)-containing melts of different basicities ($BR=\frac{mass\%CaO}{mass\%SiO_2}$)

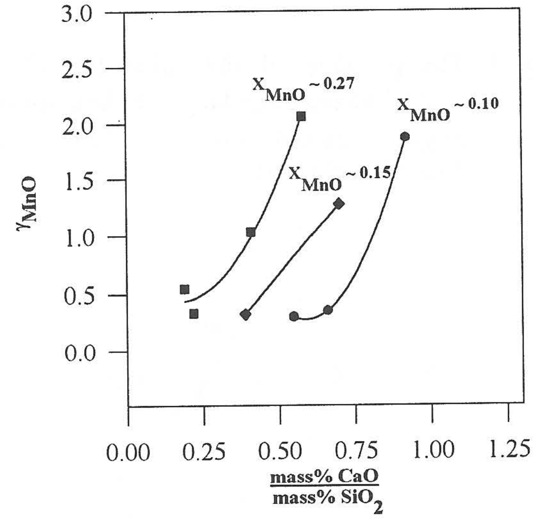

Fig. 7. Activity coefficient of MnO (γ_{MnO}) as a function of melt basicity for melts of constant MnO mole fractions

of manganese from (MnO-CrO_x-CaO-SiO_2)-containing melts into an alloy phase, the activity of MnO in the slag must be maximized without increasing its concentration. Consequently it is imperative that basic slags in which the activity coefficient of MnO is high, be used to optimize manganese recovery.

5. CONCLUSIONS

(1) Characteristic of the MnO-CrO_x-containing sub-systems which constitute the (MnO-CrO_x-CaO-SiO_2) - system, is the dominance of the $(Mn,Cr)_3O_4$ spinel phase. An increase in temperature and a lowering of the oxygen partial pressure increase the size of the spinel stability field. In the Cr_2O_3-CaO-MnO system Ca^{2+} is found in the spinel structure, while Si^{4+} is found in spinels of the Cr_2O_3-SiO_2-MnO system. More MnO can be dissolved in slags of low basicity than of high basicity, before the $(Mn,Cr)_3O_4$ spinel starts to precipitate.

(2) The 1500°C (2732°F) isotherm of the Cr_2O_3-CaO-MnO system under an oxygen pressure of $10^{-8.99}$ atm. is characterized by sub-solidus phase relations.

(3) Small all-liquid fields are found in the 1500°C (2732°F) isotherms of the Cr_2O_3-SiO_2-MnO system, due to low concentrations of Cr^{2+} in the melts under an oxygen partial pressure of $10^{-8.99}$ atm.

(4) The gas - slag - platinum equilibration technique can be used to determine activity-composition relations of MnO in (MnO - CrO_x - CaO - SiO_2) - containing melts.

(5) An increase in the concentration of MnO in the melt increases both the MnO activity and the MnO activity coefficient. For a constant MnO concentration in the melt, the activity of MnO, and therefore the activity coefficient of MnO, can be increased by increasing the basicity. Manganese recovery from (MnO-CrO_x-CaO-SiO_2)-containing melts can therefore be significantly increased by an increase in the basicity of the slag.

(6) Similarity exists between the activity-composition relations of MnO in the (MnO - CrO_x - CaO - SiO_2) - containing melts studied in this investigation, and ferromanganese slags, as well as the activity-composition relations of other divalent transition oxides e.g. CrO (8,9,10), FeO (11) and NiO (12) in silicate melts. The activity coefficient of the divalent transition oxide (γ_{MO}) can be increased significantly by an increase in the basicity of the melt in all these systems.

ACKNOWLEDGEMENT

The research was done at Mintek (The Council for Mineral Technology, Private Bag X3015, Randburg, 2125, South Africa) by the principal author. The authors wish to thank Mintek for funding this research, as well as Mr. P. Ellis and Mrs. J.A. Russell for respectively conducting the SEM and EMPA analyses.

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