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A Simple Experimental Technique for the Determination of MnO Activities at 1600°C in (MnO–MgO–SiO_2) Slags Saturated with (MnO–MgO) Solid Solutions

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Oxide mixtures containing MnO, MgO, and SiO_2 were equilibrated with manganese metal at 1600°C in MgO crucibles under an argon atmosphere, and the high-temperature phase equilibria were preserved by rapid quenching of the crucibles and their contents to room temperature. The (MnO–MgO–SiO_2) slags in equilibrium with the manganese metal were saturated with (MnO–MgO) solid solutions at 1600°C, and the chemical composition of these phases were determined by electron-microprobe analysis. As the activity–composition relationships in (MnO–MgO) solid solutions are known, the activity of MnO in the slag could be determined from the composition of the (MnO–MgO) solid solutions in equilibrium with the slag. The MnO activities of the slags determined in this way are in good agreement with the MnO activities of (MnO–MgO–SiO_2) slags determined by previous workers using the gas–slag–metal equilibrium technique.

Introduction

In steels of the SAE 200 series, nickel is partially replaced by manganese. This type of stainless steel is an attractive alternative product from an economics point of view, especially when the price of nickel is high. The nickel price has fluctuated between 3 and 22 US dollars per kilogram during the past five years[1], causing instability in the price of stainless steel. Such price instability can, to some extent, be counteracted by the production of SAE 200-type stainless steels. Manganese ore is freely available on the local market and, with the exciting prospect of a direct route for the production of stainless steel, it is evidently of great importance that information should be available on the thermodynamic behaviour of manganese oxide in slags that are likely to be used in the production of stainless steel. Such information can be used to optimize the metallurgical refining process. There is little information in the literature[2] on the thermodynamics of MnO in silicate-slag systems at 1600°C, and there is consequently much incentive to determine the activity of MnO in slags of industrial interest.

Background

The governing equation for the determination of the activity of MnO (a_{MnO}) in silicate melts is

$$(Mn)_{alloy} + \tfrac{1}{2}[O_2] \rightleftarrows <MnO>_{slag} \qquad [1]$$

where < >, [ ], and ( ) denote the solid, gas, and liquid phases respectively. The equilibrium constant with reference to pure solid MnO can be expressed as

$$K = \frac{a_{<MnO>}}{a_{(Mn)} \cdot \left(P_{O_2}\right)^{1/2}} \quad . \qquad [2]$$

The change in standard free energy (ΔG^o) for the reaction depicted by equation [1] is $-2{,}41795 \times 10^5$ J/mol[2]. In equation [2] there are three unknowns: the activity of manganese in the alloy (a_{Mn}) the oxygen partial pressure (P_{O_2}), and the activity of MnO in the slag (a_{MnO}).

Various techniques have been proposed and used to determine the activity of MnO in slags. In one technique[3-7], the molten slag is equilibrated with a manganese alloy for which the activity–composition relationships have been established previously, for example Pt–Mn. Equilibration is done in an atmosphere of known oxygen potential, and the Mn content of the Pt–Mn alloy is determined after equilibration. The activity of MnO can then be calculated from equation [2]. A knowledge of the prevailing oxygen potential in the system is usually acquired in one of two ways. The oxygen potential can be fixed by use of a gas mixture of known oxygen activity or, if the oxygen potential is not fixed, it can be measured instantaneously with an electrochemical oxygen probe. However, if the oxygen potential is fixed by use of a gas mixture, equilibrium between the gas, slag, and metal phases is achieved only after reaction periods varying between 12 and 48 hours[3-7].

If the electrochemical technique is used to determine the prevailing oxygen potential within the melt, reaction periods of only 30 to 60 minutes are required to establish

equilibrium between the slag and the metal[8-12].

A third method can be employed for the determination of the activity of MnO in silicate slags. The slag phase can be saturated with, and brought into equilibrium with, an MnO-containing solid solution of which the activity–composition relationship is known, and the activity of MnO in the slag can then be calculated from the relationship

$$a_{MnO}(\text{slag}) = a_{MnO}(\text{solid sol.}), \quad [3]$$

where a_{MnO}(slag) and a_{MnO}(solid sol.) are respectively the activities of MnO in the slag and solid-solution phases with reference to pure solid MnO. If this partially molten slag–solid solution system is equilibrated with an Mn-containing alloy of which the activity–composition relationships are not known but the oxygen partial pressure is known, then the a_{Mn} in the alloy can readily be calculated from equation [2]. Alternatively, if the a_{Mn} in the metal is known, the oxygen partial pressure of the system can be calculated.

The aim of the present study was to determine the activity of MnO in partially liquid (MnO–MgO–SiO_2) slags. These slags were saturated with (MnO–MgO) solid solutions, and were brought into equilibrium with manganese metal at 1600°C. The activity–composition relationships in (MnO–MgO) solid solutions, recently determined by Tsai[3], were then used to calculate a_{MnO} in the slag from equation [3] and the oxygen potential of the system from equation [2]. The activities of MnO determined by this experimental technique, where the slag was in equilibrium with Mn metal as well as with (MnO–MgO) solid solutions, were compared with the experimental findings of previous researchers[6,7] who used the gas–slag–metal equilibrium technique in which the oxygen partial pressure was fixed and the a_{Mn} in the alloy known.

The experimental technique used in this study could be utilized very elegantly to determine the feasibility and accuracy of the electrochemical measuring technique. The partial pressure of oxygen determined by the use of electrochemical oxygen probes can be compared with that calculated in this study, since the melts are in equilibrium with Mn and the activity of MnO in the melts is known. Should it be possible to accurately verify the ability of electrochemical probes to determine the oxygen potential in these Mn–MnO–MgO silicate-slag systems, the electrochemical technique could easily be expanded to melts where the activity of MnO is not known.

Experimental Procedure

Reagent-grade oxides supplied by Merck (Pty) Ltd and Sarchem (Pty) Ltd were used as starting materials, and the various slags were prepared by carefully weighing the exact amount of each reagent. The oxide mixtures were ground under acetone to a particle size of less than 300 μm in an agate mortar. Then, 1 g of each of the oxide mixtures and manganese metal powder were mixed thoroughly before equilibration, and were placed in a magnesia crucible (outside diameter 16 mm, inside diameter 10 mm, and height 20 mm). The initial oxide mixtures were chosen so that the crystalline phases of the slags would be at least 25 per cent when equilibrium between the slag, the solid solution, and the metal was attained[13]. This choice ensured that some of the (MnO–MgO) solid solution in equilibrium with the slag precipitated onto the walls of the MgO crucible to form a protective layer between the slag and the crucible, thereby minimizing interaction with the crucible.

The porosity of commercially available MgO crucibles is approximately 25 per cent, and preliminary tests showed that the slag and metal penetrated these crucibles and destroyed their integrity. It was therefore necessary to manufacture MgO crucibles with a lower porosity in the laboratory. This was accomplished in the following manner.

'Seawater' MgO, which contained approximately 3 per cent Al_2O_3, supplied by Vereeniging Refractories (Pty) Ltd as ball-mill fines, was ground to a particle size of less than 100 μm. A slip, containing 0,2 ml of ethanol per gram of MgO, was then slipcast into a plaster mould. The wall thickness of the eventual MgO crucible casting was determined by the contact time of the slip with the mould before decantation, and this contact period varied between 1 and 5 seconds to yield a wall thickness of approximately 1 to 2 mm. The plaster mould, which consisted of two symmetrical parts, was then carefully removed from the crucible casting. The casting was allowed to dry for 24 hours at room temperature before it was heated at a rate of 100°C per hour to 1700°C, sintered for 2 hours, and then cooled slowly. The porosity of the crucibles manufactured in this way was approximately 15 per cent, and evaluation tests indicated that the crucible contained the slag and metal satisfactorily and that little interaction between the slag–metal and the crucible occurred at 1600°C.

The slag and the metal were equilibrated within these magnesia crucibles in a vertical molybdenum-wound resistance furnace containing an alumina reaction tube and equipped with a PID temperature controller. High-purity argon gas was flushed through the alumina reaction tube and the MgO crucible containing the metal and the slag, which was suspended in a molybdenum wire basket as shown schematically in Figure 1. The molybdenum basket was suspended by a thin molybdenum wire (0,3 mm

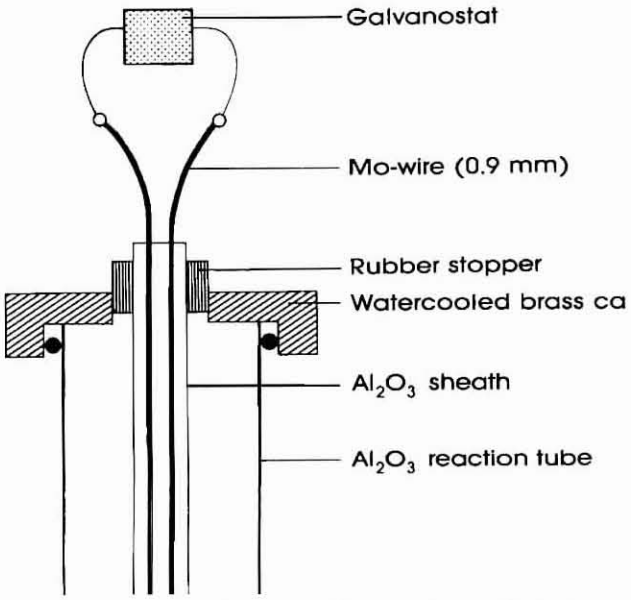

FIGURE 1. Schematic illustration of the crucible assembly for the quenching experiments

diameter), which, in turn, was fixed at the ends of two molybdenum extension wires of 0,9 mm diameter as shown in the diagram. These wires were protected by an alumina sheath, and the whole assembly was lowered slowly into the hot zone of the furnace at 1600°C. The temperature was regulated within ±3°C. In order to quench the crucible, an electric current was pulsed by means of a galvanostat through the molybdenum-wire circuit, causing the thin molybdenum wire to melt at the position where it was fixed to the basket. The crucible fell under gravitational force into a water bath at room temperature, the water bath being located in a glass container and positioned at the bottom of the reaction tube.

The quenched crucible with its contents was cut in half with a diamond saw, and was then prepared for optical microscopy and electron-microprobe analysis. The chemical compositions of the individual phases were determined by use of a JEOL 733 electron microprobe at an accelerating potential of 25 kV and a beam current of 2,5 nA. The counting time varied between 60 and 100 seconds, and oxide and silicate standards were used to quantify the analyses of MnO, MgO, and SiO_2. On average, three different grains of each phase were analysed in detail.

Results and Discussion

Before the equilibrium phase relationships could be obtained, it was necessary to determine the reaction time required to establish equilibrium between the (MnO–MgO–SiO_2) slag, the (MnO–MgO) solid solution, and the manganese metal. To achieve this, slags of two different compositions containing at least 50 per cent MnO were equilibrated with manganese metal for different periods (15, 30, 60, and 120 minutes) and quenched as previously described. Metallographically prepared sections of the quenched slags were then analysed on the microprobe. The composition of the liquid slag phase in the quenched sample was determined and was found to be the same in all the samples equilibrated for 30 minutes or longer. The chemical composition of various grains of the solid solution in each sample was also determined, and it was also found to be essentially the same.

Accordingly, there is good reason to believe that a period of 30 minutes is sufficient to attain equilibrium between the slag, the solid solution, and the metal. Furthermore, the homogeneity of the (MnO–MgO) solid-solution phase equilibrated for 30 minutes was checked in a number of sequential analyses with an electron-microprobe beam along straight lines in several directions across the exposed surface of several grains of the solid solution. No significant deviations in the composition of the solid solutions were observed, confirming that equilibrium between the slag and the metal is attained within 30 minutes. However, a reaction time of 60 minutes was used in all subsequent experiments to ensure that equilibrium was attained.

An example of a back-scattered electron image of a quenched sample is shown in Figure 2. Three different phases are clearly discernible. The white phase consists of Mn metal droplets, while the darker-grey, spherical phase represents the (MnO–MgO) solid solution. The solid solution and the manganese metal are embedded in the slag, the colour of which is slightly darker than that of the solid solution.

If a proper interpretation is to be given to the metallographic features in these samples, it is essential that the structure observed at room temperature is indeed representative of the phase equilibria that existed at 1600°C. This prerequisite deserves some comment with regard to the experimental procedure followed in this study. It is of the utmost importance that the mass and volume of the crucible, and of its contents, should be minimized to ensure that the phases that are in equilibrium at 1600°C are retained upon quenching to room temperature. Should the samples not be quenched rapidly enough from 1600°C, the liquid slag will crystallize partially and the composition of the slag phase will not be homogeneous. However, extreme care was taken in this study to ensure a sufficiently rapid quenching rate, and the homogeneity of the phases achieved upon quenching, as determined by the microprobe analyses, indicated that the quenching rate was indeed rapid enough to fulfil this requirement.

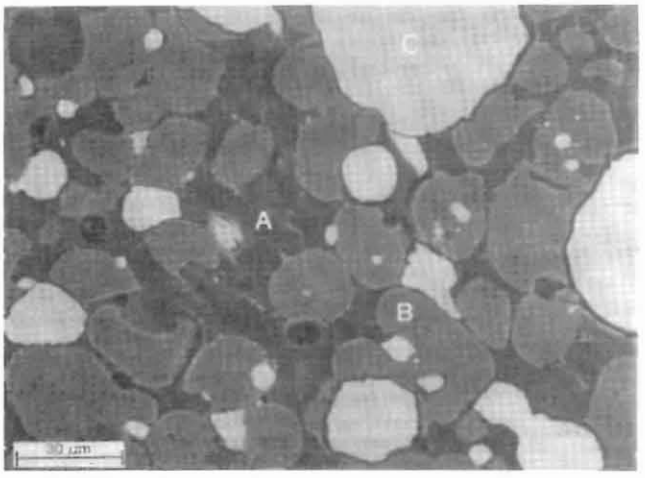

FIGURE 2. Back-scattered electron image of a quenched slag sample, showing the phases in equilibrium at 1600°C:
A = Quenched liquid slag
B = (MnO–MgO) solid solution
C = Quenched liquid manganese metal

The chemical compositions of the different oxide mixtures used as feed materials are summarized in Table I and are superimposed in Figure 3 on an isothermal section at 1600°C of the MnO–MgO–SiO_2 system proposed by Glasser and Osborn[13]. The mixtures 3M1, 3M2, and 3M3 were selected to fall within the phase field where the (MnO–MgO) solid solution and the liquid are stable and in equilibrium at 1600°C, while mixture 3M4 was selected to fall within the phase field where the olivine, the (MnO–MgO) solid solution, and the liquid are stable. Mixture 3M6 was chosen to contain the olivine and the liquid at equilibrium.

TABLE I
CHEMICAL COMPOSITIONS OF STARTING OXIDE MIXTURES AND THE EXPECTED PHASE CONSTITUTIONS AT 1600°C

	3M1	3M2	3M3	3M4	3M6
MgO, %	7	18	25	30	30
MnO, %	77	64	55	42	32
SiO_2, %	16	18	20	28	38
Metal added, %	50	50	50	50	50
Expected phases at equilibrium	$(MnO\text{-}MgO)_{ss}$+ liquid	$(MnO\text{-}MgO)_{ss}$+ liquid	$(MnO\text{-}MgO)_{ss}$+ liquid	$(MnO\text{-}MgO)_{ss}$+ liquid	Olivine+ liquid

The compositions of the liquid, olivine, and solid solutions of the different quenched samples are summarized in Table II and are also shown in Figure 3. Al_2O_3 levels of up to 5 per cent by mass were detected in some of the liquid slags, the compositions of these slag phases being indicated by triangles in Figure 3. (The alumina content of the liquid slag probably originated from the MgO crucible, because the MgO powder used in the manufacture of the crucibles contained approximately 4 per cent alumina by mass.) The slag compositions indicated by the solid circles within the centre of the triangles were used in the construction of a liquidus curve. The liquidus curves determined by Glasser and Osborn[13] are also shown in Figure 3, and there is reasonably good agreement with the results of the present study, indicating that the limited presence of Al_2O_3 in the slags of this study did not result in a serious discrepancy. Conjugation lines determined in this study, which link the compositions of the equilibrium slag and solid solution at 1600°C are also shown. It is evident that the compositions of both the final slag and the solid-solution phases of mixtures 3M1, 3M2, and 3M3 were enriched in MgO compared with the starting mixtures. This does not apply to mixtures 3M4 and 3M6, which were chosen to contain olivine at equilibrium. The higher MgO content in the final slag and the solid-solution phases of mixtures 3M1, 3M2, and 3M3 is probably due to the initial reaction of the MgO crucible with the liquid slag. However, a protective layer of (MnO–MgO) solid solution precipitated on the crucible wall as the reaction proceeded until equilibrium was attained. A conjugation line between the solid solution and the liquid, obtained by extrapolation of Glasser and Osborn's data[13] to 1600°C, is also shown in Figure 3, and this conjugation line is likewise in good agreement with the results of the present study.

The activity of MnO in solid solutions of MnO and MgO at 1600°C has been determined by Tsai[3], and his results are presented in Figure 4. Tsai's data were used to determine the activity of MnO in the slag from equation [3], and these activities are summarized in Table III.

TABLE II
COMPOSITIONS OF THE EQUILIBRIUM PHASES OF THE SAMPLES THAT WERE IN EQUILIBRIUM WITH MANGANESE METAL AT 1600°C

	3M1		3M2		3M3	
	Liquid	Solid soln	Liquid	Solid soln	Liquid	Solid soln
MgO, %	9,3	15,2	16,1	31,1	20,9	42,5
	(0,2)	(0,3)	(0,1)	(0,7)	(1,2)	(1,5)
MnO, %	58,0	84,8	50,3	68,9	46,8	57,5
	(0,3)	(0,3)	(0,9)	(0,7)	(2,1)	(1,5)
SiO_2, %	28,5	—	29,9	—	30,0	—
	(0,9)		(1,4)		(1,1)	
Al_2O_3, %	4,2	—	3,7	—	2,3	—
	(0,8)		(1,0)		(0,9)	

	3M4			3M6	
	Liquid	Solid soln	Olivine	Liquid	Olivine
MgO, %	24,4	53,0	41,1	20,6	42,0
	(1,2)	(0,2)	(0,1)	(0,8)	(0,6)
MnO, %	44,6	47,0	20,1	43,1	19,1
	(1,2)	(0,2)	(0,2)	(2,3)	(0,7)
SiO_2, %	29,2	—	38,8	31,1	38,9
	(0,6)		(0,1)	(2,1)	(0,0)
Al_2O_3, %	1,8	—	—	5,2	—
	(0,8)			(0,3)	

Figures in brackets indicate standard deviation

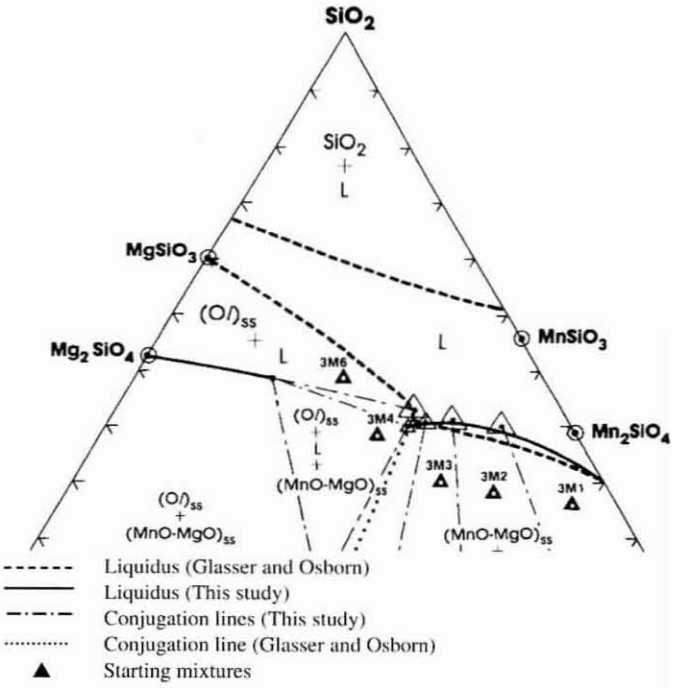

FIGURE 3. Equilibrium phase compositions in the system MnO–MgO–SiO_2 in contact with metallic manganese at 1600°C as determined in this study compared with those obtained by Glasser and Osborn

TABLE III
NORMALIZED COMPOSITION OF THE LIQUID PHASE IN EQUILIBRIUM WITH THE SOLID SOLUTION AND MANGANESE METAL (MOLAR FRACTIONS), THE MnO CONTENT OF THE SOLID SOLUTION, THE ACTIVITY OF MnO, AND THE CALCULATED P_{O_2} VALUES OF THESE SLAGS.

Mixture no.	N_{MnO}	N_{SiO_2}	N_{MgO}	$N_{(MnO)}$ solid sol.	a_{MnO}	P_{O_2} [atm.]
3M1	0,528	0,300	0,172	0,76	0,78	$1,983 \times 10^{-14}$
3M2	0,427	0,307	0,266	0,56	0,62	$1,253 \times 10^{-14}$
3M3	0,388	0,295	0,317	0,44	0,54	$9,502 \times 10^{-15}$
3M4	0,361	0,285	0,354	0,34	0,46	$6,895 \times 10^{-15}$

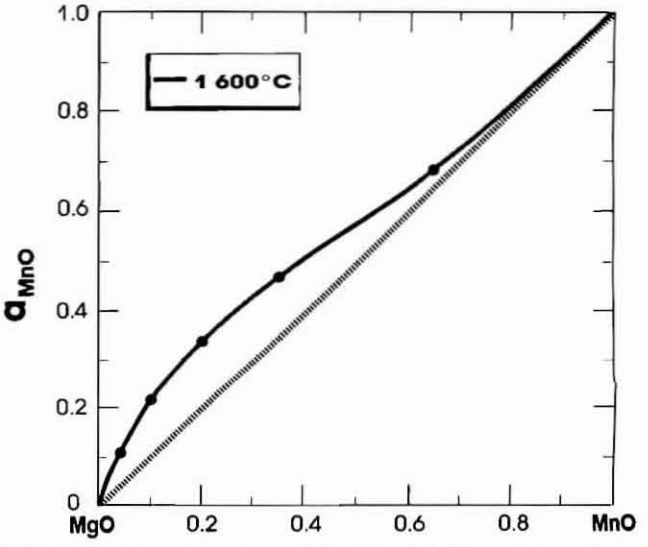

FIGURE 4. Activity–composition relationships of MnO in (MnO–MgO) solid solutions at 1600°C (after Tsai[3])

The activity of MnO in the slag is shown in Figure 5 as a function of the molar fraction of MnO. The activity of MnO in slags in the MnO–MgO–SiO_2 system at 1600°C had not been determined previously and, for the sake of comparison, the results obtained by Mehta and Richardson[6] at 1650°C are included in Figure 5. The activities determined in this study are in good agreement with those determined by Mehta and Richardson for slags with similar chemical compositions. The composition of the liquid in the MnO–SiO_2 binary system, where MnO saturation at 1600°C is obtained, as determined by Glasser[14], is also shown in Figure 5. This value is also in good agreement with the value determined in the present study by extrapolation of the experimental results.

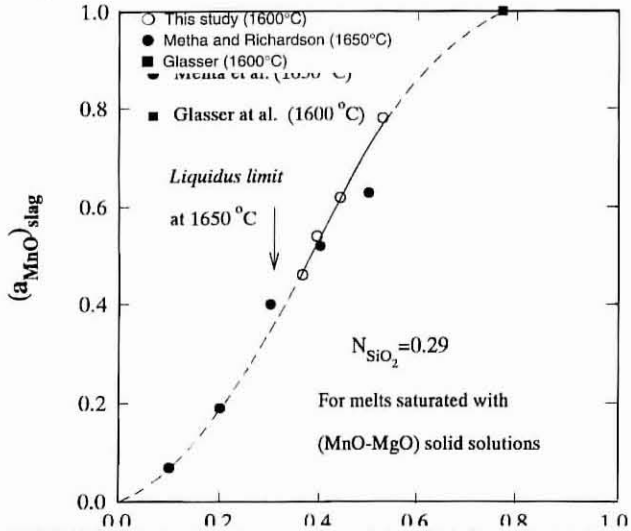

FIGURE 5. Relationships between the activity of MnO and the MnO content of (MnO–MgO–SiO_2) slags saturated with (MnO–MgO) solid solutions at 1600°C

The activity of MnO as a function of the molar fraction of MnO in the binary MnO–SiO_2 system determined at 1650°C by Abraham *et al.*[7] is shown in Figure 6. The effect of CaO additions to the MnO–SiO_2 systems on the activity of MnO is highlighted, and shows that CaO increases the activity of MnO. The results of the present study are also shown in this diagram and indicate that additions of MgO also increase the activity of MnO.

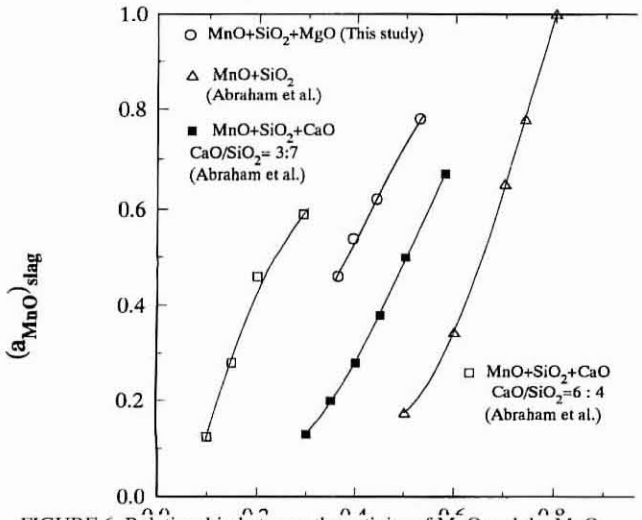

FIGURE 6. Relationship between the activity of MnO and the MnO content of different MnO-containing slags at 1600°C

The saturation limit of MnO in the liquid component of some (MnO–MgO–SiO_2) slags determined in the present study is shown in Figure 7 as a function of the MgO-to-MnO ratio at a constant SiO_2 content of approximately 30 per cent by mass. As expected, the solubility of MnO in the slag decreases with an increase in the MgO-to-MnO ratio. The solubility of MnO will have to be limited in slags that are to be used in the production of steels of high manganese content. The results of the present study, as shown in Figure 7, are consequently experimental confirmation that this can be achieved through an increase in the MgO-to-MnO ratio in the slag.

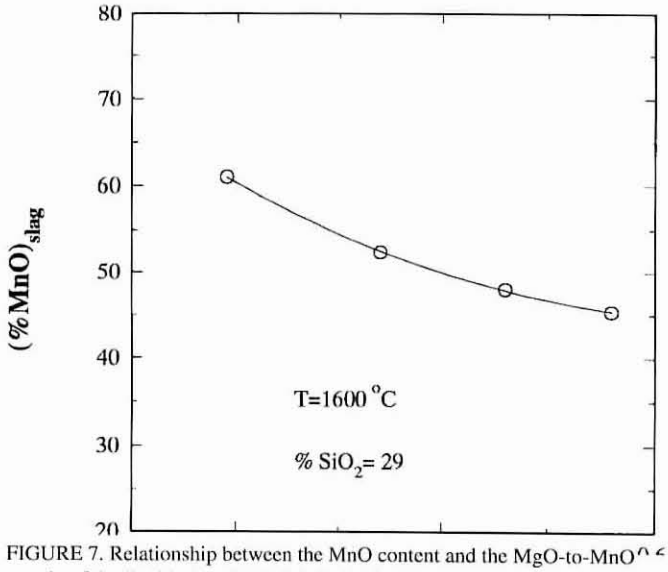

FIGURE 7. Relationship between the MnO content and the MgO-to-MnO ratio of the liquid phase in the MnO–MgO–SiO_2 system at 1600°C as determined in this study

In conclusion, it was shown that the activity of MnO in (MnO–MgO–SiO_2) slags that are saturated with (MnO–MgO) solid solutions and in contact with pure molten manganese metal can be determined from a determination of the chemical compositions of the constituent phases in equilibrium at high temperature. This finding is in good agreement with the results of previous workers, who employed different experimental techniques. The results obtained in this study can also be used to determine the oxygen potential of a slag–metal system under investigation. Accordingly, the experimental techniques used in this study can be utilized very elegantly to evaluate the accuracy of the electrochemical technique to measure the oxygen activity in liquid slags of similar composition. The partial pressure of oxygen determined with the aid of electrochemical oxygen probes can be compared with the values determined in this study, since the molten slag is in equilibrium with liquid Mn metal and the activity of the MnO in the melts has been established. The use of the electrochemical technique could then easily be expanded to melts where the activity of MnO is not known.

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