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The thermodynamic activity of MnO in stainless steel type slags

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The thermodynamic activity of MnO was measured in MnO-CaO-MgO-SiO_2 slags that are typically encountered in the production of manganese containing stainless steels. Gas equilibration-quenching technique was employed in measuring the activities.

Activity of Mn in Pt-Mn alloys were redetermined at 1600°C which reconfirmed earlier results of strong negative deviations. MnO activities were then measured by equilibrating slags of various compositions based on a statistical experimental design procedure with Pt-Mn alloys under controlled partial pressure of oxygen in MnO saturated platinum crucibles at 1600°C.

Activities of MnO were found to increase with increasing concentration of MnO, basicity and CaO to MgO ratio. Two multi-coefficient repression models were developed to predict the activities and activity coefficients of MnO in slags at 1600°C.

Keywords: activity, MnO, slag.

Introduction

Manganese is one of the most widely used alloying materials in modern steel production and has also found applications in the new group of stainless steels containing both manganese and nitrogen. In the production of such manganese containing steels, Mn will distribute itself between the slag and metal phases and thus the MnO in the slag will reach a certain activity value. The optimization of the recovery of manganese in stainless steel making is essential for the refining process to be efficient. Physicochemically, the efficiency depends on the thermodynamic properties of the slag and metal phase through the activities of MnO in the slag and Mn in the metal. Although there is sufficient literature on thermodynamic activity of MnO in MnO-SiO_2 binary[1], in blast furnace slags, in CaO-SiO_2-MgO, MnO-SiO_2-MnO ternaries[2–13] and in ferromanganese smelting slags[14–15], the literature on the thermodynamic activity of MnO in manganese stainless steel type is practically non-existent. Activity-composition relationships in Pt-Mn binary systems are well established[16–18]. This metallic system was re-investigated in the present study for calibration purposes at 1600°C, since the slags were equilibrated with Pt-strips (which became Pt-Mn alloys) during experimental measurements. Thus, this work was undertaken to determine the activities of MnO in stainless steel type slags and to develop empirical model equations based on experimental results to predict the MnO activities in the composition range studied.

Experimental procedure

The gas equilibration-quenching technique was used for the determination of the activity-composition relations both in Pt-Mn alloys and in stainless steel slags in the present study. The merits of choosing this particular method and the details of the experimental set-up and procedure have been discussed in detail in an earlier publication[15] and they will not be repeated here, however the following have to be recorded.

The platinum strips (4mm x 4mm square cut from 0.025 mm thick foil) were equilibrated with slag (or pure MnO in the Pt-Mn binary measurements) in a Pt-crucible (10 mm ID x 17 mm height and 0.125 mm wall thickness) under a certain partial pressure of oxygen imposed by gas mixtures of CO and CO_2.

Prior to any experimental run, the Pt-crucibles were equilibrated and thus saturated with pure MnO at the chosen gas mixture and temperature, thus preventing the transfer of Mn into the Pt-crucible instead of the Pt-strips.

The gas equilibration technique in this study makes use of the following equilibrium reaction:

$$MnO(s.\ell) = Mn(\ell) + \tfrac{1}{2}O_2(g) \qquad [1]$$

for which the equilibrium constant is given by

$$K = a_{Mn}\sqrt{P'_{O_2}}\,/\,a'_{MnO} \qquad [2]$$

if pure MnO is used in the equilibration (e.g Pt-Mn binary system). If a slag containing MnO is used, the equilibrium constant will be:

$$K = a_{Mn}\sqrt{P'_{O_2}}\,/\,a_{MnO} \qquad [3]$$

Since the equilibrium constants given by Equations [2] and [3] are identical, rearrangement of the above two questions yields:

$$a_{MnO} = \sqrt{P_{O_2}/P'_{O_2}}\,a'_{MnO}\left(a_{Mn}/a'_{Mn}\right) \qquad [4]$$

and when $a_{Mn} = a'_{Mn}$, Equation [4] reduces to:

$$a_{MnO} = \sqrt{P_{O_2}/P'_{O_2}}\,a'_{MnO} \qquad [5]$$

Therefore, P_{O_2} is the partial pressure of oxygen prevailing at the time of the experiment (generated here by CO-CO_2

gas mixture), P'_{O_2} is the pressure of oxygen that would be in equilibrium with pure MnO and an alloy that contains the same amount of manganese as was formed in the slag experiment, hence $a'_{Mn} = a_{Mn'}$, and P'_{O_2} is thus from the Pt-Mn binary in equilibrium with pure MnO at the same temperature, and a'_{MnO} is the activity of the stoichiometric MnO in the non-stoichiometric oxide that would be in equilibrium with P'_{O_2}.

Values of P'_{O_2} and a'_{Mn} have been measured by Richardson *et al.*[16] and by Davies and Richardson[19] respectively. In previous studies[15,18] it was well established that at 1600°C, the equilibrium between Pt-Mn binary alloys and pure Mn was reached within 8 hours when Pt-strips utilized were 0.051 mm thick. In this study thinner Pt-strips (0.025 mm) were used, but to ensure that equilibrium was reached experiments were run for 12 hours. The Pt-Mn samples were analysed with microprobe using wavelength dispersive spectrometers. In all the samples, including the slag experiments, the alloys were completely homogeneous indicating that equilibrium was reached. The equilibration time for slags containing MnO and Pt-strips were determined by three independent experiments conducted for six, eight and fifteen hours at 1600°C. The concentrations of Pt and Mn in these strips were identical within analytical error ranges, and again the concentration profiles were very flat. For convenience reasons, however, the slag experiments were also conducted for 12 hours. All the Pt-strips were analysed by electron microprobe for Pt, Mn and Si where Si levels were always below the detection limit of 0.02%. The slags were ground in an agate mortar and analysed by ICP Emission spectroscopy. The slags consisted of a glass matrix with some precipitates.

The slag compositions were in the following range: CaO: 40–50%, MgO: 12–20%, SiO_2: 39–45%, MnO: 0.5–5%.

Within this range, 18 initial slag samples were prepared based on a statistical experimental design procedure[20–21] which, in a four component system as in here, is represented by hyperpolyhedron (convex polyhedron) in three dimensional format. The experimental points (the slag compositions) are represented by the vertices, face centroids and overall centroid of the polyhedron. This statistical experimental design approach minimizes the number of highly costly experiments and allows response-surface model equations to be developed. Hence a quadratic regression equation was developed for activity (and activity coefficient) of MnO with respect to mole fraction of slag constituents.

Results and discussion

Activity-composition relations in the solid solution region of the Pt-Mn binary system were redetermined at 1600°C. The oxygen partial pressure used in these experiments varied between 2.57×10^{-4} atm and 1.00×10^{-7} atms. In Figure 1, the activity coefficient of Mn at 1600°C is plotted against its mole fraction, together with earlier result of Rao and Gaskell[18] in the form of the following equation:

$$\ell n\gamma_{Mn} = -0.2405 - 0.881925X^2{}_{Pt} - 29.2948X^3{}_{Pt} + 20.3603X^4{}_{Pt} \qquad [6]$$

It is quite clear from Figure 1 that the agreement between this work and the earlier results Rao and Gaskell[18] is very good at 1600°C. Thus Equation [6] was used in this study to calculate the activity coefficient and hence activity of Mn that would be necessary for calculating the $a_{Mn\,O}$ values in the slag compositions.

In total twenty two successful experimental runs were carried out in order to determine MnO activities in slags at 1600°C. The basicity ratio of the final equilibrated slags varied between 0.92 and 1.44. The partial pressure of oxygen was fixed at 7.89×10^{-7} atm in the slag experiments. Activities and activity coefficients of MnO in these CaO-MgO-SiO_2-MnO slags were calculated with respect to both pure solid MnO and pure liquid MnO as the standard states. Regression models based on the results of the present work using pure liquid MnO as the standard state were developed to predict the activity coefficients and activities of MnO as a function of composition within the slag composition range studied.

The two quadratic multivariable regression model equations derived from the complete data of 22 experimental runs had very high correlation coefficients ($R^2=0.8669$ for activity coefficients, $R^2=0.9107$ for activities) indicating an excellent fit to the experimental data. The independent variables were the mole fractions of CaO, MnO, SiO_2 and MgO in the slags. The regressions were carried out using routines from the Statistical Analysis Software (SAS) system. The model equations are:

$$\ln\gamma_{MnO(\ell)} = -110.1215 + 142.5293X_{MgO} + 131.4409X_{SiO_2} + 131.7369X_{MnO} + 184.5480X^2_{CaO} + 27.0040\,X_{CaO}\,X_{MnO} \qquad [7]$$

$$a_{MnO(\ell)} = -14.0592 + 19.3288X_{CaO} + 26.2086X_{MgO} + 17.3279X_{MnO} - 8.7712X^2_{MgO} + 18.6412\,X^2_{SiO_2} - 19.3972X_{CaO}\,X_{MnO} \qquad [8]$$

It must be noted that due to the nature of the model it is not advisable to use these equations if the slag composition falls outside the range mentioned earlier.

A typical plot illustrating the increase of activity of MnO with increasing mole fraction of MnO is shown in Figure 2. The symbols represent the experimental values, while the solid line represents the predicted values calculated from Equation [8]. In this figure the experimental points selected have similar basicity and CaO to MgO ratios (although in a certain range).

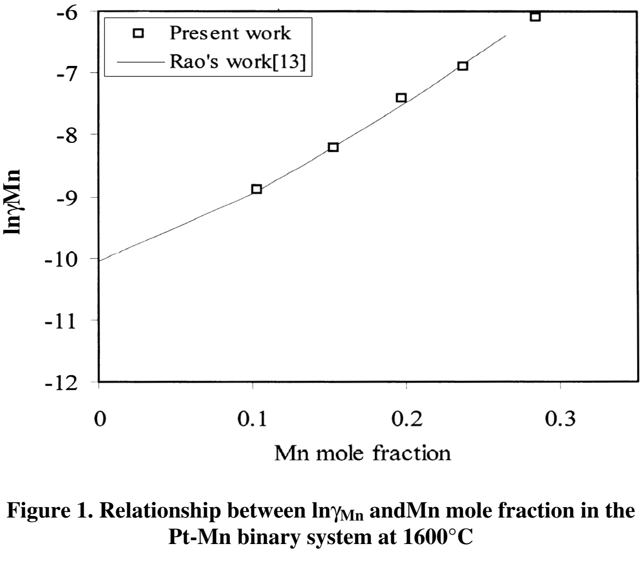

Figure 1. Relationship between $\ln\gamma_{Mn}$ andMn mole fraction in the Pt-Mn binary system at 1600°C

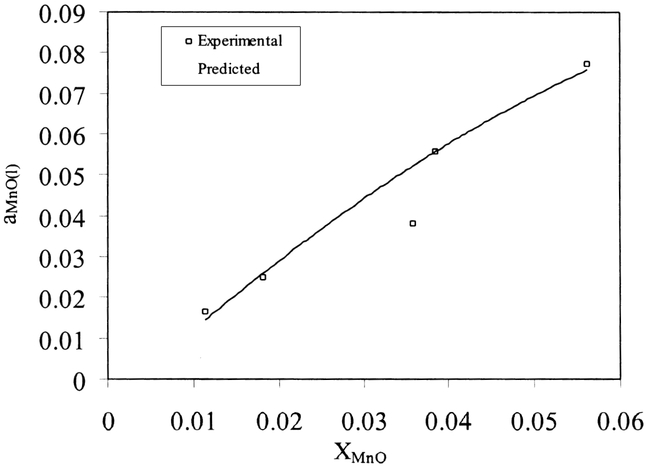

Figure 2. The variation of MnO activity with composition in MnO-CaO-MgO-SiO_2 slags at 1600°C, B=1.06–1.12, CaO:MgO=2.65–3.35

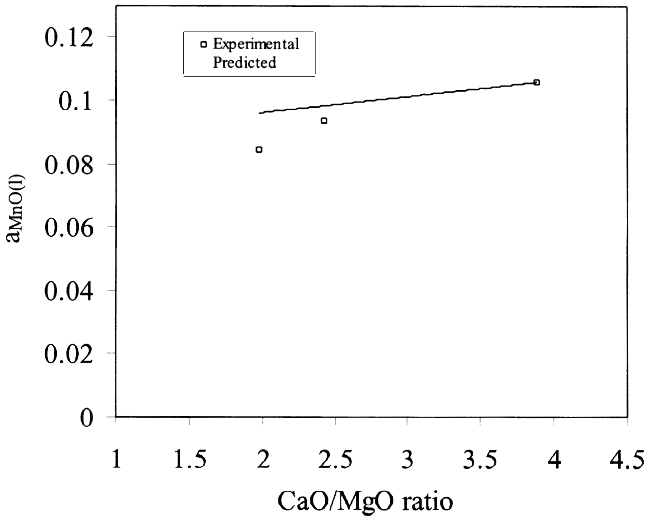

Figure 3. The effect of CaO to MgO ratio on the activity of MnO in MnO-CaO-MgO-SiO_2 slags at 1600°C with B=1.33–1.38, X_{MnO}=0.026–0.042

As can be seen the agreement between calculated and measured values is very good. The results are also in good agreement with previous studies[2–15] which reported that activity of MnO increases with its concentration. Obviously this is an expected behaviour since at a given concentration of MnO in the slags, a certain proportion of Mn^{2+} ions will be associated with the silicate anions, and a certain proportion of them will be associated with free oxygen ions. An increase in the concentration of MnO in the slag will further break down the network structure causing an increase in the number of free oxygen ions. Silicate anionic groups are preferentially associated with Ca^{2+} and Mg^{2+} ions and metal ions such as Mn^{2+}, due to their preference for free oxygen ions, will be associated with free oxygen ions which will be reflected as an increase in MnO activity.

In Figure 3, the effect of CaO to MgO ratio on the activity of MnO at a certain basicity ratio range defined as (% CaO + %MgO)/%SiO$_2$, and certain x_{MnO} range is illustrated. The CaO to MgO ratio has a slight effect in increasing the MnO activities which is in accord with the work of Cengizler and Eric[15]. When the free energy of formation of the orthosilicates Ca_2SiO_4, Mg_2SiO_4 and $CaMgSiO_4$ are taken into consideration, it can easily be seen that Ca_2SiO_4 has the most negative free energy of formation[22–25] followed by $CaMgSiO_4$ and Mg_2SiO_4. In other words, the interaction of Ca^{2+} ions with silica is stronger than those of mixed Ca^{2+} and Mg^{2+} ions and Mg^{2+}. Thus one can conclude that an increase in the amount of CaO can lead to an increase in the tendency of formation of Ca_2SiO_4 arthosilicate. Therefore Mn^{2+} ions become freer, i.e. less associated with silicate network, and the a_{MnO} values tend to increase.

Figure 4 illustrates the dominant effect of basicity in increasing the activity of MnO in accord with previous studies[14–15]. This can be explained in a very similar way in terms of modern slag theory. At low basicities almost all the metal cations are associated with the large silicate anionic groups and only a very few free oxygen ions exist. In other words, at low basicities, the silica network is not

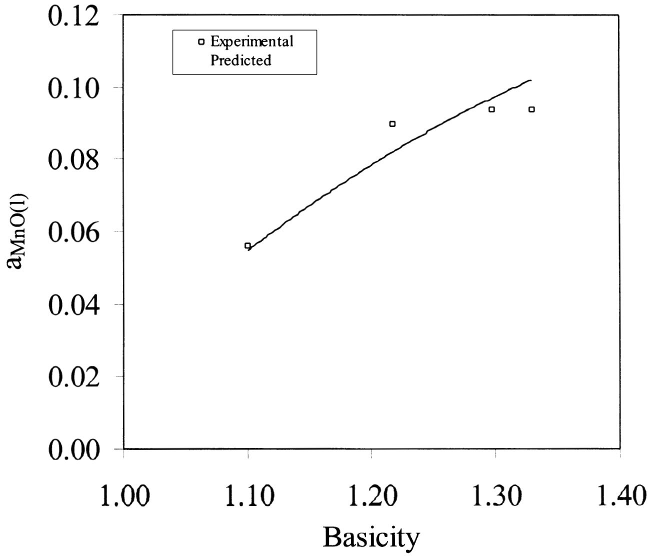

Figure 4. The effect of basicity on activity of MnO in MnO-CaO-MgO-SiO_2 slags at 1600°C with X_{MnO}=0.0385–0.0424, CaO:MgO=2.42–3.44

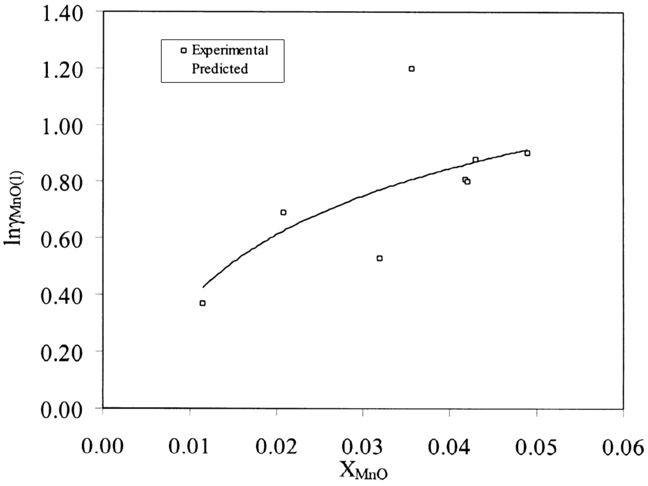

Figure 5. The variation of activity coefficient of MnO with composition in MnO-CaO-MgO-SiO_2 slags at 1600°C, CaO:MgO=2.3–2.6, B=1.12–1.135

disrupted leading to low MnO activities. As the concentration of basic oxides increases, the silicate network is broken up into smaller anionic groups and the proportion of free oxygen ions begins to increase. Divalent cations like Ca^{2+} and Mg^{2+} because of their higher interaction with silicates ions are preferentially associated with silicate anions and thus Mn^{2+} ions will have less degree of association with silicate ions, become freer and hence MnO activities increase as basicity increases. There is also the fact that at higher basicity values, the slag liquidus temperatures tend to increase which would also result in an increase in MnO activity.

Turkdogan[11]claimed that the activity coefficient of MnO is not affected by its own concentration, but Cengizler and Eric[15] showed in their study on thermodynamics of ferromanganese smelting slags that the activity coefficient of MnO increases significantly with an increase in its mole fraction. Figure 5 is a typical plot from this work, indicating the increase in MnO activity coefficient with an increase in its mole fraction in accord with previous work[15]. The results of Turkdogan[11] are also out of line with those calculated from the results of Filer and Darken[10] by Abraham *et al.*[16]. Moreover, Turkdogan[11] was also unable to show the temperature dependence of activity of MnO shown subsequently by Abraham *et al.*[16] and Mehta and Richardson[3]. The activity coefficient, in this case that of MnO is also a measure or indicator of interactions between ions and atoms and thus should be affected by composition. The increase in the activity coefficient of MnO in stainless steel type slags with increasing concentration (with basicity and CaO to MgO ratio as well) can again be explained by the use of modern slag theory in exactly the same manner as done above for the case of activities. In Figure 6, the natural logarithm of the activity coefficient of MnO in the form of iso-activity coefficient curves is shown in the liquid slag region of the quaternary $CaO-MgO-SiO_2-MnO$ system. Due to the low concentration of MnO, the representation of the system was reduced into a pseudo-ternary (CaO+MgO) $-MgO-SiO_2$ system.

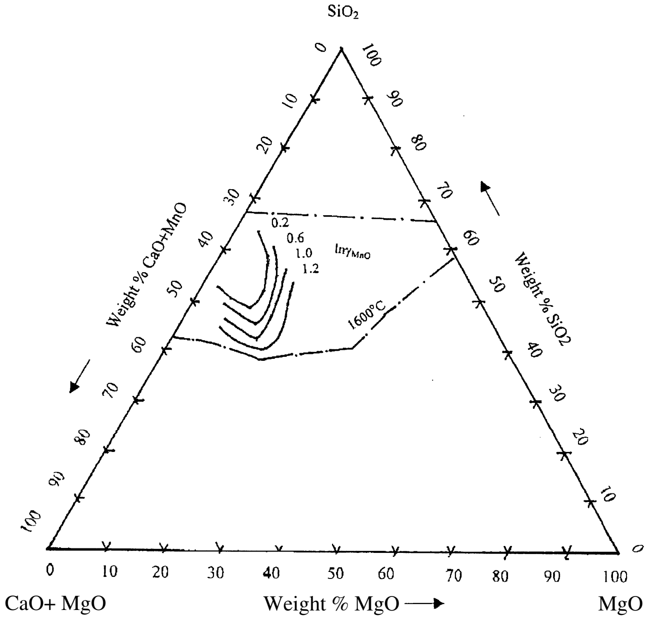

Figure 6. Iso-activity coefficient curves of MnO in pseudo-ternary system $(CaO+MnO)-MgO-SiO_2$ in the liquid slag region at 1600°C (Reference state: pure liquid MnO)

Summary and conclusions

This study was carried out to determine the activity of MnO in synthetic $MnO-CaO-MgO-SiO_2$ slags that are typically encountered in the production of stainless steels containing manganese. Classical gas equilibration-quenching technique was used to measure the MnO activities utilizing Pt-strips and Pt crucibles under a fixed oxygen partial pressure at 1600°C. The initial slag sample compositions were determined using a statistical experimental design procedure. Two quadratic multi-variable regression models were derived using the SAS system for predicting the activities and activity coefficients of MnO in these slags from the measured MnO activity data. The results indicate that the activity of MnO (and its activity coefficient) increases with increases in its own concentration, basicity ratio and CaO to MgO ratio.

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