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Thermodynamics of the MnO-containing slags and equilibrium relations associated with Mn ferroalloy productions

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Slag-metal and slag-metal-gas heterogeneous equilibria involving MnO-containing slags have been simulated using recently developed Mn-based alloy and IRSID oxide thermochemical databases. A large number of experimental equilibrium data have been used to verify the calculation results. The experimental slag-metal and slag-metal-gas equilibria in MnO-SiO_2 binary, MnO-SiO_2-CaO and MnO-SiO_2-Al_2O_3 ternary, MnO-SiO_2-CaO-Al_2O_3 quaternary and MnO-SiO_2-CaO-Al_2O_3-MgO higher-order system can be reproduced within experimental uncertainties. The influence of temperature, CO partial pressure and slag chemistry on the Mn- and Si-distribution equilibria have been quantitatively evaluated. This leads to a sound basis for optimizing the manganese ferroalloy production processes.

Key words: MnO-containing slag, manganese ferroalloy, equilibrium simulation, thermochemical database

Introduction

In production of high carbon ferromanganese and silicomanganese alloys, slag always plays an important role in the distribution of elements among different phases. The main oxide components in raw materials are MnO, SiO_2, CaO, Al_2O_3 and MgO. Manganese and silicon oxides are simultaneously reduced by 'carbon', either as graphite or in SiC

$$(MnO)+\text{'}C\text{'}=\underline{Mn}+CO_{(g)} \qquad [1]$$

$$(SiO_2)+2\text{'}C\text{'}=\underline{Si}+2CO_{(g)} \qquad [2]$$

A combination of these two reactions gives distributions of manganese and silicon between metal and slag phases

$$2(MnO)+\underline{Si}=2\underline{Mn}+(SiO_2) \qquad [3]$$

Parentheses denote species present in the slag phase and underlines in the alloy phase. Oxides CaO, Al_2O_3 and MgO are thermochemically stable at operating temperatures and go almost completely to the slag phase. Even though these slag-forming components do not take part in the reduction process, they are of great importance for the thermochemical and thermophysical properties of slag phase.

Laboratory investigations were carried out to study the distribution equilibria for the high carbon ferromanganese and silicomanganese alloys[1–10]. Although these experimental results may provide a basic image of equilibrium compositions for the given system, it is still difficult to give exact quantities and compositions of reduction products. The reason is that the final state of a given system is dependent not only on the chemical equilibrium, but also on the restriction of stoichiometry, i.e. materials balance.

Computational thermodynamics is a powerful tool for quantitative characterization of important equilibrium relations for production of manganese ferroalloys. Chemical equilibrium and mass balance are automatically satisfied through both mathematical and thermodynamic solutions. Based on existing experimental data, the model is capable of using thermodynamic interpolations and extrapolations to predict equilibrium relations in regions where there is a lack of experimental knowledge.

In the present paper, the computerized thermochemical databases developed for manganese ferroalloys are briefly introduced. The computation results will be extensively verified by experimental data in various MnO-containing slags. The influence of several operating parameters is predicted quantitatively. Applications of the present thermochemical databases to predict the distribution equilibria in high carbon ferromanganese and silicomanganese alloys processes will finally be demonstrated.

Thermochemical databases

Successful thermodynamic simulation depends strongly on reliable thermodynamic descriptions of the non-ideal metallic and oxide solutions. A recent investigation[11] has shown that the cellular mode[12–13] is capable of giving good fits to the measured MnO and SiO^2 activities in the MnO-SiO_2-CaO-Al_2O_3-MgO liquid slags. Application of the modified quasi-chemical model[14] with a given set of published parameters leads to inaccurate description of the thermodynamic properties in the low MnO domain of liquid MnO-SiO_2-CaO-Al_2O_3 slags.

By extensive examination of measured thermochemical properties and phase equilibrium data relevant to the MnO-SiO_2 binary, MnO-SiO_2-CaO and MnO-SiO_2-Al_2O_3 ternary,

$MnO-SiO_2-CaO-Al_2O_3$ quaternary and $MnO-SiO_2-CaO-Al_2O_3-MgO$ higher-order system, the present authors[18] have concluded that the quasi-chemical model works better than the cell model for description of phase diagrams. The cell model cannot represent correctly phase equilibria in the area of mullite saturation. On the other hand, the quasi-chemical model fails to reproduce measured activity and equilibrium data in the low MnO domain of liquid $MnO-SiO_2-CaO-Al_2O_3-MgO$ solution. This has recently been confirmed by MnO-activity measurements[17] in the $MnO-SiO_2-Al_2O_3$ system. Since the low MnO region is essential for simulation of the silicomanganese smelting process, it has been decided to use the IRSID cell model in this work.

A private thermochemical database for the $MnO-SiO_2-CaO-Al_2O_3-MgO-FeO$ oxide system, including liquid slag solution and stoichiometric compounds, has been made based mainly on the published IRSID model parameters[12–13]. The new database has been successfully implemented in the FactSage commercial software[15] for phase equilibrium and thermodynamic property calculations. It is worth mentioning that the re-evaluated parameters[11] for the MnO-CaO system cannot generate a correct MnO-CaO phase diagram. The reason is that the authors[11] misused the activity data of the solid $MnO-SiO_2$ monoxide phase to evaluate the properties of liquid solution, which is not stable at temperatures below 1840°C. Contrarily, phase relations in the MnO-CaO binary system can be fairly reproduced using the original model parameters[12-13]. It has thus been decided to use the original model parameters[12–13] of the MnO-CaO system in the present investigation.

A thermochemical database that covers all stable phases relevant to the Mn-Fe-Si-C system has previously been developed by the present authors[19]. This database has been used to compute the metal-slag and metal-slag-gas equilibria. The alloy database has been developed mainly on the basis of the SGTE databank[16], but many modifications have been made in order to fit the reliable experimental data. For example, the SGTE databank gives much higher values of the carbon solubility in the Mn-(Fe)-Si-C melts, especially in the low Si composition region, as can be seen from Figure 1(a). Such problems have successfully been excluded by applying the new alloy database, see Figure 1(b).

Distribution equilibria between carbon-saturated Mn-(Fe)-Si-C alloys and various MnO-containing slags were measured under different conditions by a number of authors[1–8]. Metal-slag equilibria between carbon-free Mn-Fe-Si alloys and silicate slags containing various amounts of MnO, CaO and Al_2O_3 were also reported in the literature[9–10]. These experimental data provide a good basis for examination of the results of the present model calculations. Calculated MnO and SiO_2 contents of slags equilibrated with carbon-saturated Mn-(Fe)-Si-C alloys under CO atmosphere are compared with measured data and showed in Figure 2(a) and (b), respectively. The x-axis represents the measured values while the y-axis represents the calculated ones. A similar comparison of Si contents in the metal phase is given in Figure 2(c). Calculated results are in good agreement with the experimental values over a broad composition and temperature range. A comparison of the computed and measured distribution data between carbon-free Mn-(Fe)-Si alloy and $MnO-SiO_2-CaO-Al_2O_3$ slags is presented in Figure 2(d). Also, here good agreement exists between the calculated and measured equilibrium contents.

Discussions

The successful reproduction of all experimental results leads to a sound basis for quantitative evaluation of the influence of operating parameters in the production of ferromanganese alloys. The calculations have been carried out using the FactSage software package[15]. Figure 3 demonstrates the effect of temperature for the Si distribution equilibria between $Mn-Si-C_{sat}$ alloys and the $MnO-SiO_2-CaO-Al_2O_3$ slags with fixed CaO/Al_2O_3 mass ratio at 3.

The metal-slag reaction is little dependent on the temperature. For every 100 degree of increase in temperature, an increase of 0.8–1.2 mass per cent Si in the

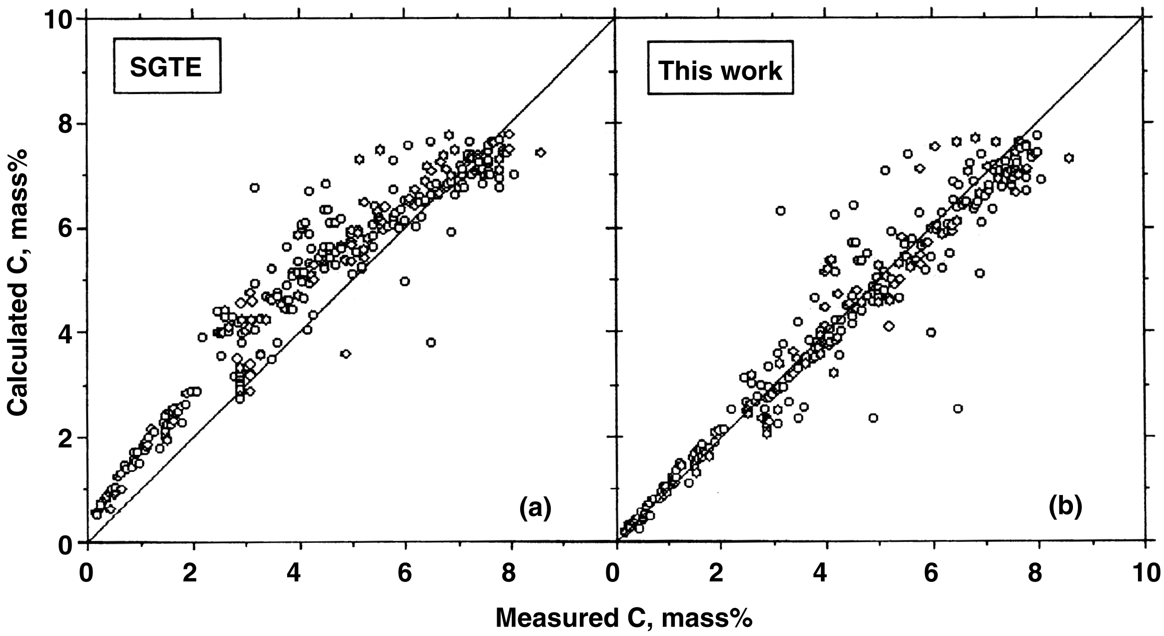

Figure 1. Comparison of the calculated and measured carbon solubility in the Mn-(Fe)-Si alloys (a)SGTE databank (b) the present database

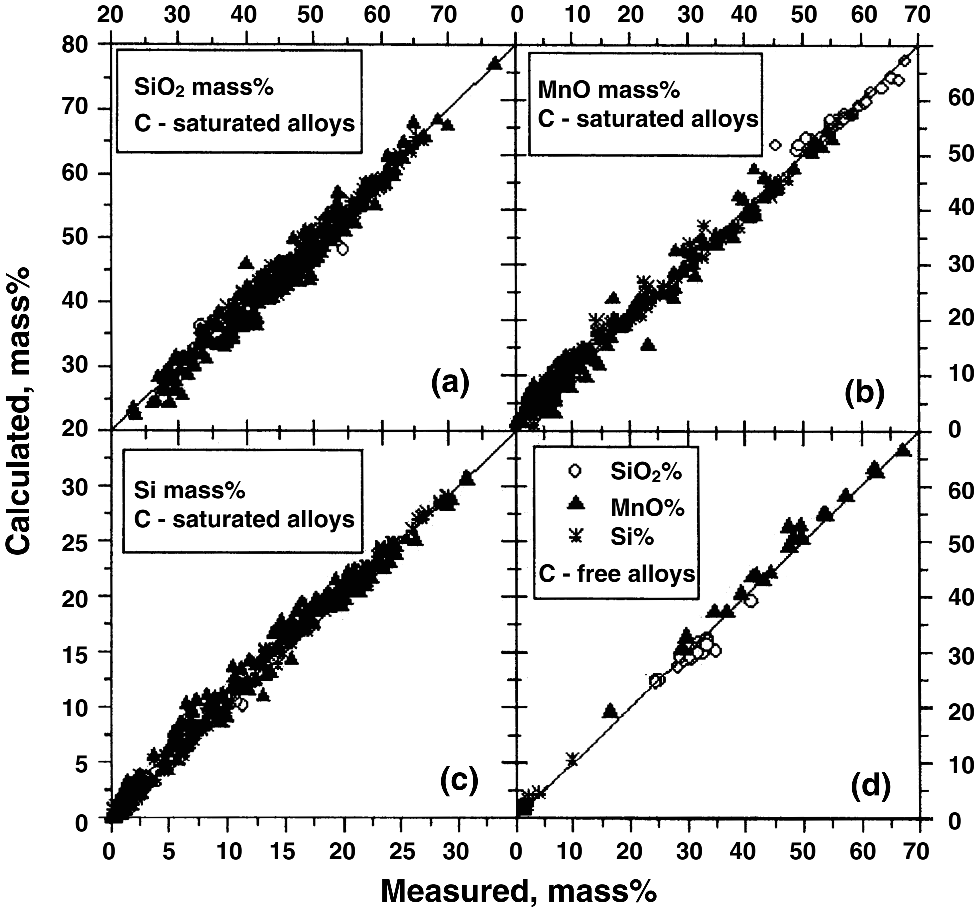

Figure 2. Comparison between measured and calculated equilibrium contents

alloy phase takes place in the higher MnO contents region. However, temperature has no virtual influence on the equilibrated Si compositions when β-SiC replaces graphite as the stable phase. In contrast to the relatively small effect on the metal-slag equilibrium, temperature is of great importance for the equilibrium relations when the gaseous species are taken into account. The MnO concentrations of slags shift notably to the lower region with increasing temperatures. Increasing temperature has the advantage of lowering the manganese losses in the slag phase.

The effect of the CO partial pressure is illustrated in Figure 4. The measured data are also presented for comparison. A reduction of the CO partial pressure from one to one-third of an atmosphere is equivalent to an increase in temperature around 100°C. The influence of the CO partial pressure was estimated experimentally to be equivalent to an increase in temperature of about 50–70°C for the metal-slag-gas equilibria. Reduction of the CO partial pressure benefits the recovery of manganese to a great extent. The blast furnace process is an industrial example of low CO pressure operation.

In order to describe the compositions and properties of high carbon ferromanganese slags, the term 'basicity' is often applied. It is defined as[21] the mass ratio of 'basic' to 'acid' oxides in the slag phase

$$B = \left(100 - \%MnO - \%SiO_2 - \%Al_2O_3\right) / \left(\%SiO_2 - \%Al_2O_3\right) \qquad [4]$$

It has been stated[21] that the basicity is defined by the applied raw materials and will not change in the course of reduction.

Calculated 'reduction paths' of two charge-mixtures are presented in Figure 5. The calculations have been carried out at every 5 degree temperature interval. Solid lines represent the metal-slag-gas equilibrium compositions at given temperatures. Dashed lines indicate the equilibrium compositions of metal-slag equilibria at 1500°C. The thick lines represent the 'reduction paths' of certain charge-mixtures. Dash-dot lines are the 'basicity' lines defined only by the compositions of charge-mixtures. For a given charge-mixture, its 'reduction path' follows the basicity line at temperatures below 1450°C. Since reduction of SiO_2 requires relative higher temperature, only MnO is substantially reduced. The 'reduction path' will deviate increasingly from the basicity line at higher temperatures due to the occurence of silica reduction.

According to equilibrium calculations, a charge-mixture having basicity 0.46 will be reduced to 40% MnO at 1400°C and to 28% MnO at 1450°C. If the basicity of charge-mixture is adjusted to 0.9 by adding fluxes, MnO contents will finally be reduced to 24% MnO at 1400°C and to 16% MnO at 1450°C. Increasing basicity is an efficient way of improving the manganese recovery.

It has been shown[3] that the silicon distribution equilibria for the silicomanganese slags can be well characterized by introducing of the R-value, which is defined as the mass ratio of the sum of basic oxides to Al_2O_3. Figure 6 shows the computed Si distribution equilibria between MnO-SiO_2-CaO-Al_2O_3-MgO ($CaO/MgO=2.5$) slags and Mn-Fe-Si-C_{sat} ($Mn/Fe=7$) alloys equilibrated with CO gas. The characterizing ability of the R-value is clearly demonstrated in the diagram. For a given SiO_2 composition, slag with

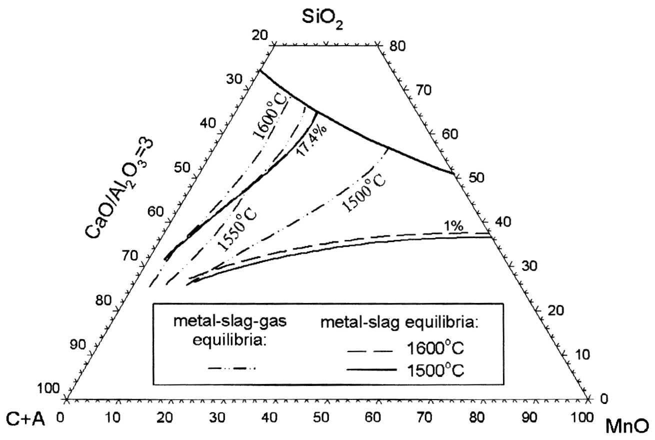

Figure 3. Effect of temperature on the Si distribution equilibria between $MnO-SiO_2-CaO-Al_2O_3$ ($CaO/Al_2O_3=3$) slags and Mn-Si-C_{stat} alloys

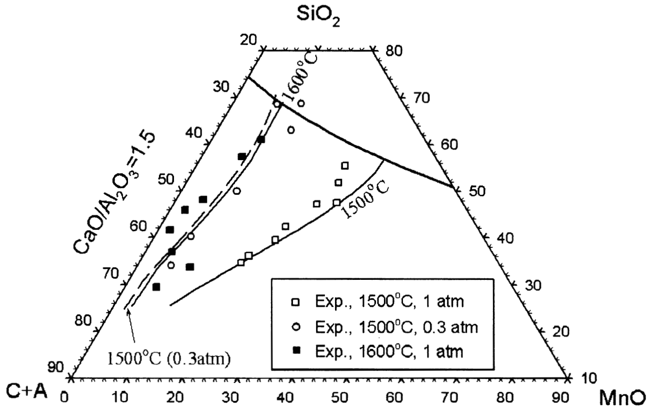

Figure 4. Effect of CO partial pressure on the metal-slag-gas equilibria in the $SiO_2-MnO-CaO-Al_2O_3$ ($CaO/Al_2O_3=1.5$) system

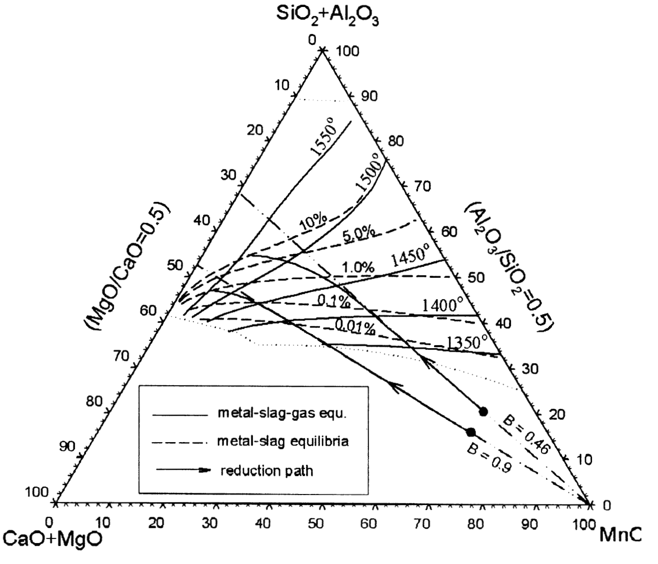

Figure 5. Calculated equilibrium relations associated with the high carbon ferromanganese smelting process

lower R-value has the ability of giving higher Si content in the alloy phase.

The silicon content of the alloys increases fast with increasing silica in the slag up to 16.8% Si. Then follows a slow increase until silica saturation is reached. The change in slope is a result of carbon being replaced by silicon carbide as reducing agent. The amphoteric effect of Al_2O_3 is also clearly illustrated at point A. Addition of Al_2O_3 to the basic slags results in increasing MnO in the slag phase, whereas addition to more acid slags has the opposite effect. The change between 'acid' and 'basic' slags takes place at about 54% SiO_2 for this particular case.

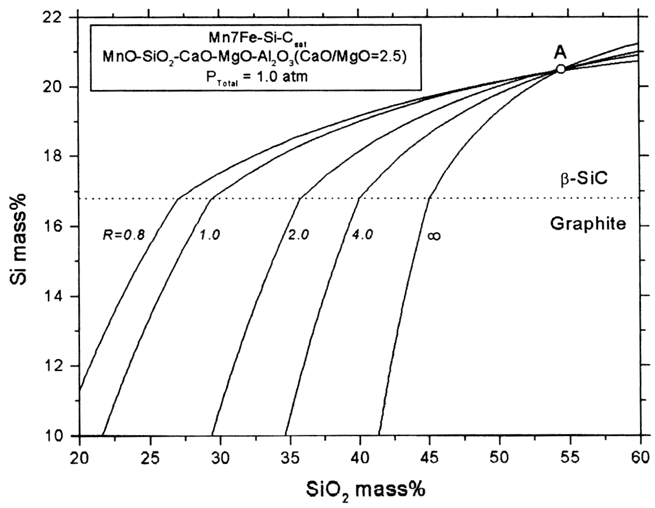

Figure 6. Distribution of silicon as function of the mass ratio $R=(CaO+MgO)/Al_2O_3$ at 1600°C

Conclusions

Heterogeneous equilibria related to the production of manganese ferroalloys have been simulated using recently developed thermochemical databases. The IRSID cellular mode has been chosen to represent thermodynamic properties of the molten slag phase while the compound energy formalism has been used for the Mn-Fe-Si-C system. More then 650 measured equilibrium data have been applied to verify and calibrate the model calculations.

The influence of several operating parameters relevant to the production of ferromanganese alloys has been quantitatively evaluated. The computation results have been confirmed by the experimental observations. This leads to a sound basis for prediction of equilibrium relations in regions where there is a lack of experimental knowledge.

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