COMPUTER SIMULATION OF THE EQUILIBRIUM RELATIONS ASSOCIATED WITH THE PRODUCTION OF MANGANESE FERROALLOYS

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ABSTRACT

The complex heterogeneous equilibria associated with the production of manganese ferroalloys have been simulated by employing recently developed thermochemical databases. The non-ideal Mn-Fe-Si-C alloy and the $MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaO\text{-}MgO\text{-}FeO$ *slag system have been modelled separately by the compound energy and cellular model. A large number of experimental thermodynamic and phase-equilibrium data were used to evaluate the model parameters for the liquid and solid Mn-Fe-Si-C phases. In addition to the liquid metal phase, solid mixture phases occurring in the Mn-Fe-Si-C system have also been studied. Over 500 measured equilibrium data have been utilised to verify and calibrate the model calculations. The paper will present typical simulation results, from activities of components to multicomponent heterogeneous equilibria. Good agreements can be obtained for many important technological parameters such as carbon solubility, phase relations and equilibrium diagrams, element distribution as function of temperature and slag composition etc. Application of the present models to the silicomanganese production will be demonstrated in this paper.*

1. INTRODUCTION

Manganese ferroalloys are produced by carbothermic reduction of oxide ores mainly in electric submerged arc furnaces. The distributions of Mn and Si between $Mn\text{-}Fe\text{-}Si\text{-}C_{sat}$ alloys and silicate slags containing various amounts of MnO, Al_2O_3, CaO and MgO are the result of simultaneous reactions taking place inside the furnace. An understanding of these reactions can help metallurgists to predict and control the element distributions among different phases.

Extensive laboratory investigations have over years been carried out to study equilibrium relations associated with production of manganese ferroalloys[1][2][3][5][6][7]. The influence of different operating parameters was established semi-quantitatively from the experimental results. For example, the effect of temperature on metal/slag equilibrium defined as $(MnO)+\underline{Si}=(SiO_2)+\underline{Mn}$, is relatively small. Contrarily, temperature plays an important role in the metal/slag/gas equilibrium. Increasing temperature has the advantage of lowering the manganese losses in slag. For the slag chemistry, addition of Al_2O_3 to “acid” slags will result in lower MnO contents whereas addition to more basic slags has the opposite effect. Consequently, increasing of “slag basicity” can reduce considerably the MnO contents. Reduction of the CO partial pressure is equivalent in effect to increase of temperature for the metal/slag/gas equilibrium.

Thermodynamic modelling is a powerful tool for quantitative characterisation of important equilibrium information for production of manganese ferroalloys. Based on existing experimental data, the model employs thermodynamically correct interpolations and extrapolations to predict the equilibrium relations in the regions where the data do not exist. It also offers advantage to avoid some difficulties encountered during the measurements.

The objective of the present investigation has been to simulate thermodynamically the complex heterogeneous multicomponent equilibria involved in the process for production of manganese alloys by employing assessed thermochemical databases. The calculated equilibrium relations were verified and calibrated by the experimental data. Application of the present developed databases to predict equilibria in the silicomanganese smelting process is finally demonstrated.

2. THERMODYNAMIC MODELS AND DATABASES

The liquid slag and alloy are the most important phases to be taken into consideration in connection with manganese alloy smelting processes. The liquid alloy and slag phases have to be modelled separately due to the nature of these phases. In addition to the liquid phases, the solid stoichiometric compounds (C, SiC, SiO_2, MnO,…) and the non-stoichiometric mixture phases (M_xC_y carbides, monoxides, …) must be taken into account in the thermodynamic calculations.

Manganese, silicon, iron and carbon are the key components in the manganese ferroalloys. The liquid metal is normally carbon saturated in the smelting process. In order to simulate the solidification patterns of the manganese alloys and decarbonization of HC-FeMn, thermodynamic description of the solid phases is also essential. Therefore, a thermochemical database that covers all stable and metastable phases in the Mn-Fe-Si-C quaternary system was developed by the authors[11]. Excess Gibbs energy of the liquid metal phase was obtained by evaluation of measured enthalpies, activities, phase diagrams and metal/slag/gas equilibrium distribution ratios. Thermodynamic descriptions of the solid phases were mainly taken from the SGTE databank[12]. However, model parameters related to solid δ–Mn(bcc) γ–Mn(fcc) and diamond phases in the Fe-Si, Si-C, Fe-Si-C and Mn-Si-C subsystems were re-evaluated in order to fit the reliable experimental data. The liquid and the solid δ–Mn, γ–Mn, β–Mn(cbcc), α–Mn(cub) and ε–Mn(hcp) phases were treated as quaternary mixtures, whereas the $(Mn,Fe)_{23}C_6$, $(Mn,Fe)_7C_3$, $(Mn,Fe)_5C_2$, $(Mn,Fe)_3C$, (Mn,Fe)Si, $(Mn,Fe)_5Si_3$ and $(Mn,Fe)_3Si$ phases are modelled as ternaries. The sub-lattice model was employed for all the mixture phases in the Mn-Fe-Si-C system.

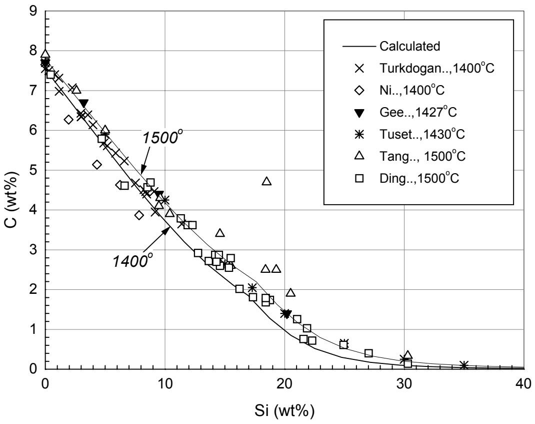
Under reducing atmosphere and at elevated temperatures, the trivalent Fe and Mn oxides go almost completely into the bivalent state. Slags can thus be represented by the MnO-SiO_2-Al_2O_3-CaO-MgO-FeO system. A computerised thermodynamic database was constructed based mainly on the published IRSID model parameters[8][9][10]. In addition to the liquid slag phase, the monoxide solids (Ca, Mn, Mg, Fe)O, also play important roles in the smelting processes[4][6][7]. Gaye and Welfringer[8] found that the (Mn, Fe, Ca)O solid solution can be simply treated as an ideal solution. This simple treatment has been extended to the (Ca, Mn, Mg, Fe)O monoxide solution in the present investigation. As illustrated by the authors[16], this treatment leads to a fair description of the experimental liquidus data in the MnO-SiO_2-Al_2O_3-CaO-MgO system. Composition variations in other solid oxides were not considered in this work. Since the calcium, aluminium and magnesium contents are negligible in the metal phase, they are assumed to only exist in the oxide phases. The gas phase is treated as an ideal solution.

In the previous studies[1][2], the equilibrium constant approach was employed to analyse and estimate the equilibrium relations. In the present investigation the Gibbs energy minimisation technique was used to calculate the most stable phase assemblies in the Mn-Si-Fe-C-Al-Ca-Mg-O system. The commercial software packages, FactSage[17] and ChemSage[18], have been used for all equilibrium calculations in this investigation. The mass balance and mass action equations are solved simultaneously to satisfy both mass conservation and thermodynamic constraints.

3. RESULTS AND DISCUSSIONS

The newly developed database was verified by comparing the calculated phase boundaries and component activities with the experimental data. Figure 1 shows that the calculated carbon solubility in the Mn-Si alloys is in good agreement with the measured values at 1400-1500^{o}C. Calculated manganese activities in the Mn-Si-C_{sat} alloys at 1500^{o}C were compared with recently measured values[14] as shown in Figure 2.

Similar verifications were carried out for the Mn-Fe-Si-C_{sat} quaternary system. It was confirmed that calculated iso-activity contours of Mn in the Mn-Fe-Si-C_{sat} alloys are in fair agreement with the measured values reported by Tanaka[13] and Olsø *et al.*[23].



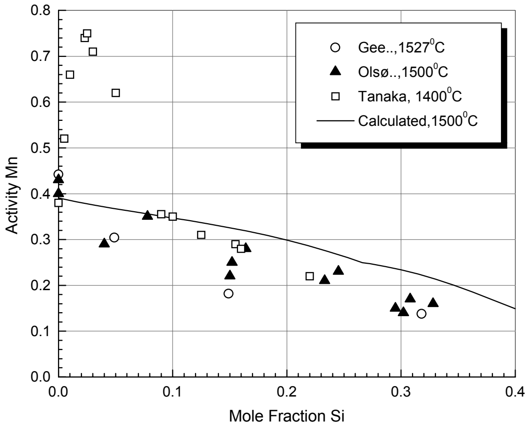


Figure 1. Comparison of calculated and measured carbon solubility in Mn-Si-C alloys at 1400 and 1500°C.

Figure 2. Comparison of calculated and measured Mn activity in Mn-Si-C_{sat} alloys at 1500°C.

Figure 3 presents as an example of the calculated liquidus surface of the Mn7Fe-Si-C (Mn/Fe=7) pseudo-ternary system. The solid lines represent univariant reactions indicating the liquidus field boundaries of the primary crystals. The dotted lines denote liquidus isotherms. The solidification path of a Mn7Fe-18%Si-2%C alloy is shown as a dashed line in this figure. The sequence of phases formed when this alloy solidifies under the so-called Scheil-cooling condition is: L → SiC → $(Mn,Fe)_5Si_3$ → Mn_7C_3 → $(Mn,Fe)_3Si$ → γ–Mn → β–Mn. Such simulations are very useful for an understanding of the important operational conditions during casting of commercial manganese ferroalloys.

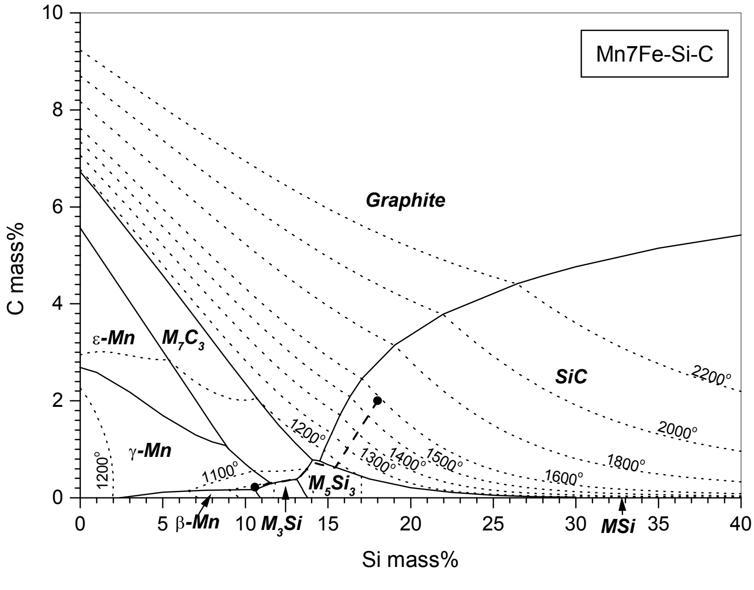
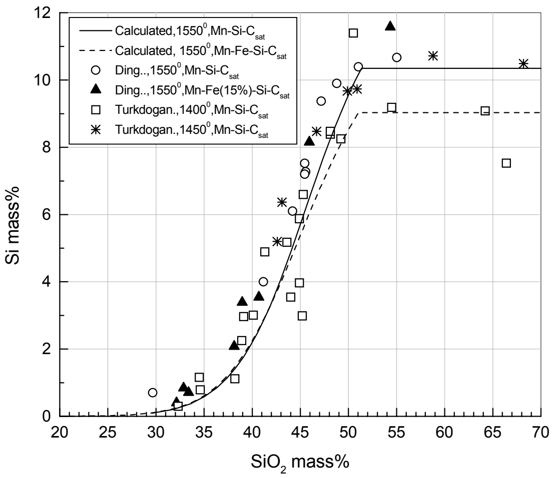


Figure 3. Calculated liquidus surface of the Mn-Fe-Si-C quaternary system at Mn/Fe=7.

The equilibrium distribution of Si between Mn-(Fe)-Si-C_{sat} alloys and binary MnO-SiO_2 slags was obtained experimentally[1][19]. Calculated results are compared with these experimental data in Figure 4. The model is capable of reproducing the experimental data within the experimental error limits.



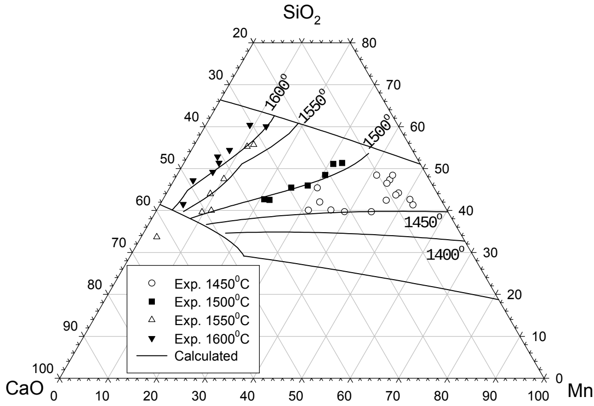
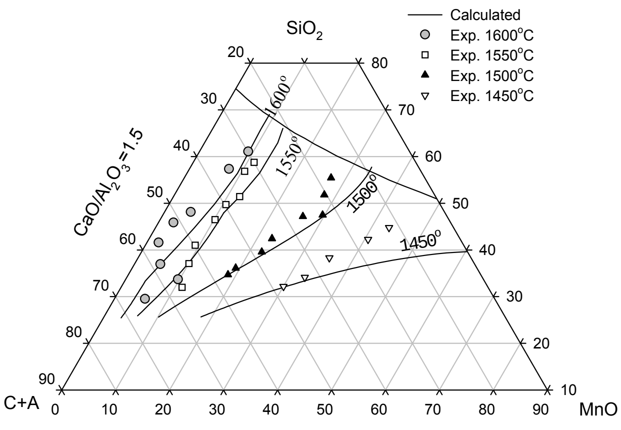


Figure 4. Comparison of experimental and calculated equilibrium relations between binary MnO-SiO$_2$ slags and Mn-(Fe)-Si-C$_{sat}$ alloys at 1550^{o}C

Figure 5. Comparison of experimental and calculated equilibrium relations for ternary MnO-SiO$_2$-CaO slags in contact with Mn-Si-C$_{sat}$ alloys at P$_{CO}$=1 atm

Chemical equilibria between ternary MnO-SiO$_2$-CaO slags and Mn-Si-C$_{sat}$ alloys at temperatures in the range 1400-1600^{o}C were studied extensively by Ding and Olsen[1][2], Turkdogan and Hancock[19], Tanaka[24], Rankin[20], Kor[21] and Tuset *et al.*[22] The experimental results of Ding and Olsen[1] were used to test the validity of the thermodynamic models. Figure 5 shows the calculated metal/slag/gas equilibrium relations together with the measured points. In the high temperature range, *i.e.* 1500-1600^{o}C, the calculated results are capable of reproducing the experimental data. At relatively lower temperatures, the measured points are very scattered due to difficulties encountered in the measurements. The model predicted values are within experimental uncertainty. The break in the curves at temperatures of 1550 and 1600^{o}C indicates the phase transformation of graphite to β-SiC.



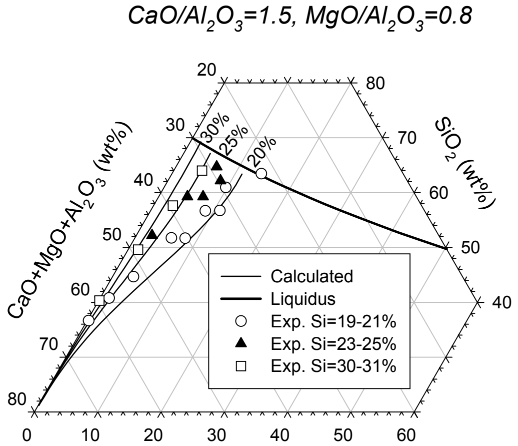


Figure 6. Comparison of experimental and calculated equilibrium relations for quaternary MnO-SiO$_2$-CaO-Al$_2$O$_3$ slags in contact with Mn-Si-C$_{sat}$ alloys.

Figure 7. Comparison of experimental and calculated Si distribution equilibria for MnO-SiO$_2$-CaO-Al$_2$O$_3$-MgO slags in contact with Mn-10%Fe-Si-C$_{sat}$ alloys.

A large amount of experimental data also exists for metal/slag and metal/slag/gas equilibria concerning quaternary MnO-SiO$_2$-CaO-Al$_2$O$_3$ slags[1][2][3]. Slag composition triangles are suitably used to show heterogeneous multicomponent equilibria graphically. MnO and SiO$_2$ each occupy one apex of the composition triangle while a combination of CaO+Al$_2$O$_3$ with fixed CaO/Al$_2$O$_3$ ratio occupies the third apex.

Figure 6 shows comparisons between calculated and measured metal/slag/gas equilibrium relations for $MnO\text{-}SiO_2\text{-}CaO\text{-}Al_2O_3$ ($CaO/Al_2O_3=1.5$) slags and Mn-Si-C_{sat} alloys. Solid lines represent calculated equilibria at P_{CO} = 1 atm. Good agreement exists between calculated and experimental data.

Si distribution equilibria are particularly important for production of silicomanganese alloys. The model predicted Si distribution equilibria for silicomanganese slags ($MnO\text{-}SiO_2\text{-}Al_2O_3\text{-}CaO\text{-}MgO$ at $CaO/Al_2O_3=1.5$, $MgO/Al_2O_3=0.8$) and Mn-Fe(10%)-Si-C_{sat} alloys are compared with measured points and shown in Figure 7. Good agreement exists between calculated and experimental data.

The measured equilibrium compositions of alloys and slags were used to calculate equilibrium compositions given by the solution models. More than 500 measured equilibrium data points were used. Calculated and measured Si and C contents in the metal phase equilibrated with various MnO-containing slags in the temperature range 1400-1600^{0}C are compared in Figure 8. The x-axis represents the measured values while the y-axis represents the model-calculated values. The calculated results give a good description of measured contents of Si and C in the metal phase. Regarding the slag phase, only calculated and measured contents of MnO and SiO_2 are compared. The result is shown in Figure 9. The calculated MnO and SiO_2 contents agree well with the experimental data for all slag systems over a broad composition and temperature range, except some data occuring for the $MnO\text{-}SiO_2\text{-}Al_2O_3$ slags. Probably this results from the inaccurate description of the $SiO_2\text{-}Al_2O_3$ binary system by the IRSID model[8][16].

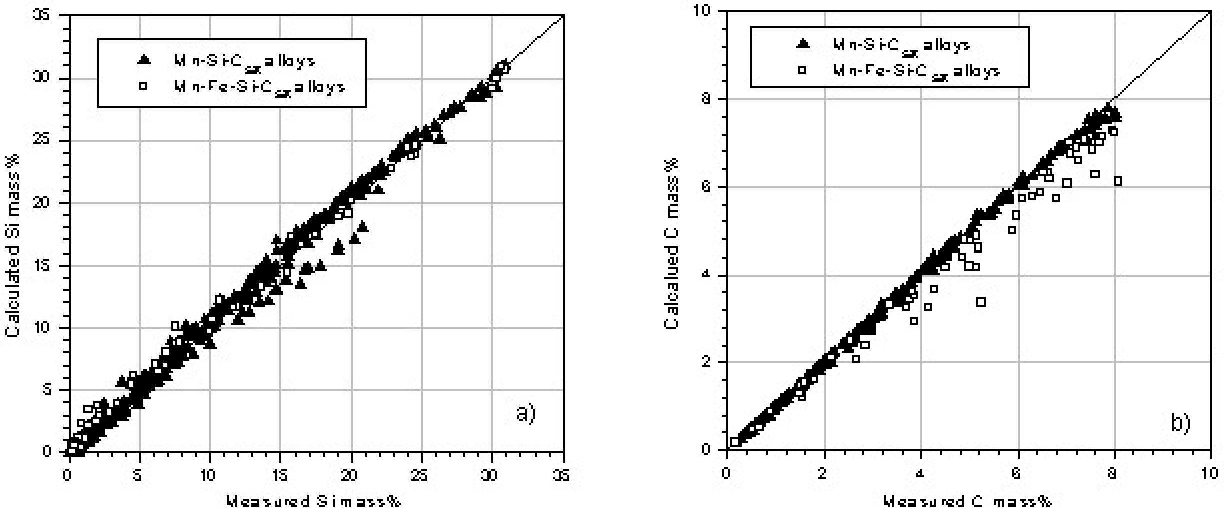


Figure 8. Comparison between calculated and experimental values of equilibrium a) Si and b) C contents in metal phase.

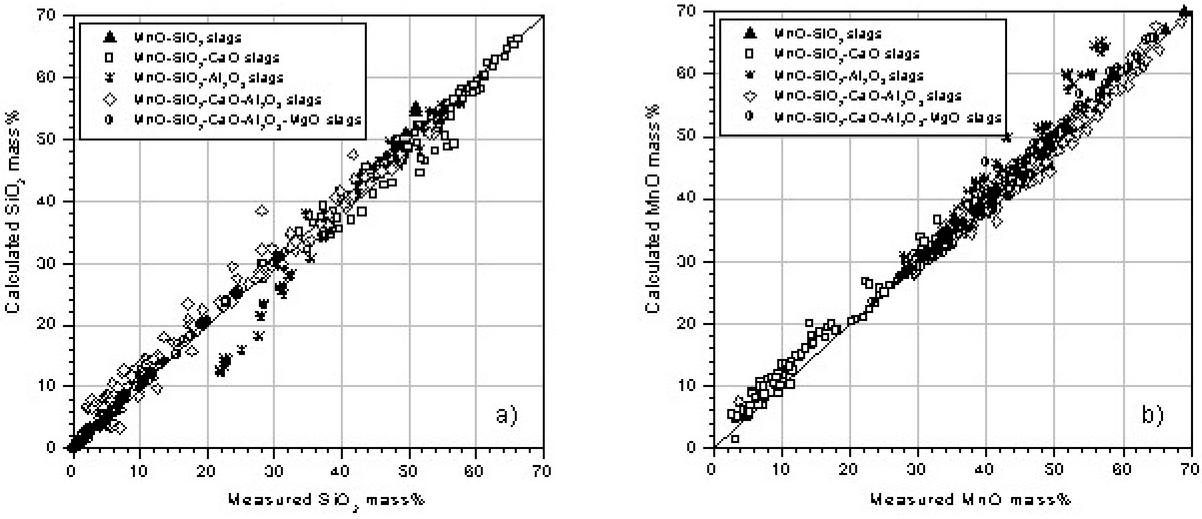


Figure 9. Comparison between calculated and experimental values of equilibrium a) SiO_2 and b) MnO contents in slag phase.

For carbothermic reduction of silicomanganese alloys, it is of particular interest to determine the maximum Si content of the metal phase. An attempt was earlier made by Ding[2] to estimate the maximum Si-content of Mn-Si-C_{sat} alloys under the assumption of silica saturation in the slag phase. It was found that a temperature of about 1680°C is required to produce an Fe-free manganese alloy with about 30wt% Si at P_{CO} = 1 atm. The result of model calculations is presented in Figure 10. As can be read from the diagram, an Mn-Si(30%)-C_{sat} alloy can be obtained at 1680°C by simultaneous carbothermic reduction of MnO and SiO_2 at unity activity of silica and P_{CO} = 1 atm. A rise of 10°C is required to obtain a Mn7Fe-Si(30%)-C_{sat} alloy, provided the slag is kept silica-saturated. Furthermore, if normal silicomanganese slags are used, having silica activities less than unity (e.g. a_{siO2}=0.2), even higher temperatures (1755°C) are needed to produce an Mn7Fe-Si(30%)-C_{sat} alloy.

The effect of CO partial pressure has been demonstrated in Figure 11. A reduction of CO partial pressure from one to one-third of an atmosphere can efficiently reduce the temperature necessary for production of a Mn7Fe-Si(30%)-C_{sat} alloy.

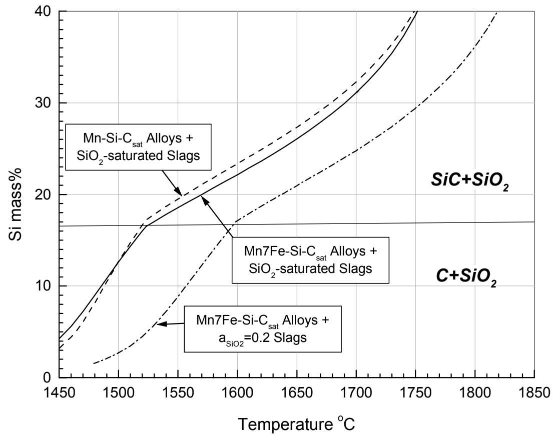


Figure 10. Calculated silicon content as function of temperature for Mn-Si-C_{sat} and Mn7Fe-Si-C_{sat} alloys in equilibrium with different slags at 1 atm

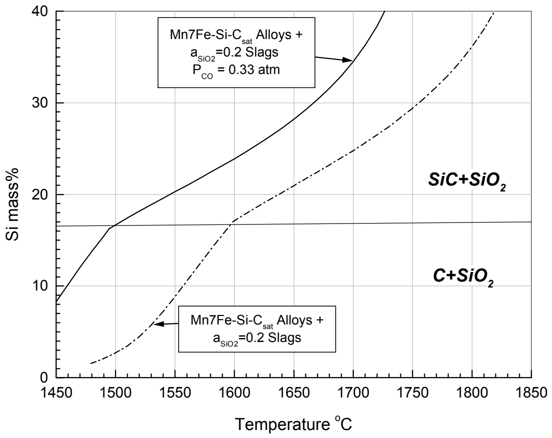


Figure 11. Calculated effect of P_{CO} on the Silicon content as function of temperature for Mn7Fe-Si-C_{sat} alloys in equilibrium with a_{SiO2}=0.2 slags

4. CONCLUSIONS

A thermochemical database that covers all stable and metastable phases in the Mn-Fe-Si-C quaternary system was developed and used to simulate the complex heterogeneous equilibria associated with production of manganese ferroalloys. A large amount of experimental equilibrium data was used to verify and calibrate the model calculations. Good agreement can be obtained for many important technological parameters such as carbon solubility, phase relations, equilibrium diagrams and element distribution as functions of temperature and slag composition. As demonstrated in the figures, the present investigation gives a good basis for predicting phase equilibria inside an industrial furnace, and may therefore provide useful information for control of slag and metal compositions and for developing new process routes.

5. REFERENCES

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