Phase Equilibria and Thermodynamic Properties of the CaO–MnO–Al₂O₃–SiO₂ System by Critical Evaluation, Modeling and Experiment

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A complete literature review, critical evaluation and thermodynamic modeling of phase diagrams and thermodynamic properties of the CaO–MnO–Al₂O₃–SiO₂ system at 1 bar pressure are presented. A few new quaternary liquidus measurements are also reported. The modeling is based solely upon model parameters obtained by critical evaluation and optimization of the four ternary subsystems. The predicted quaternary properties and phase diagrams are in very good agreement with measurements. Complex phase relationships are elucidated and discrepancies among the data are resolved. The database of model parameters can be used along with software for Gibbs energy minimization in order to calculate any phase diagram section or thermodynamic property from 25°C to above the liquidus at all compositions.

KEY WORDS: solution thermodynamics; CaO–MnO–Al₂O₃–SiO₂ system; manganese alloy production; phase equilibria.

1. Introduction

The CaO–MnO–Al₂O₃–SiO₂ system is of interest for inclusion control in Mn/Si-killed steel. Mn/Si complex deoxidation is indispensable for the production of high-value steel such as tire-cord steel, valve-spring steel and high-Ni steel (Fe–36mass%Ni Invar steel) in order to avoid the harmful effects of solid Al₂O₃ inclusions which can be formed when Al is used as deoxidizer. Al₂O₃ inclusions usually cause wire breakage during tire-cord production, where inclusions should be deformable during the wire-making process. Usually, Mn/Si deoxidation results in MnO–SiO₂(–Al₂O₃) inclusions of low melting temperature. However, the inclusions can be transformed to CaO–MnO–SiO₂–Al₂O₃ inclusions by reaction with top slag in the ladle. In order to control inclusions accurately, inclusion engineering, based on the thermodynamic relations between inclusions and liquid steel, should be carried out during the secondary refining stage in the ladle and tundish. The CaO–MnO–SiO₂–Al₂O₃ system is also a key system in the production of manganese alloys, and is of geological importance.

As part of a wider research project to extend the F*A*C*T oxide databases,¹⁾ the CaO–MnO–Al₂O₃–SiO₂ system has been completely evaluated and thermodynamically optimized.

In a thermodynamic “optimization” of a system, all available thermodynamic and phase-equilibrium data are evaluated simultaneously in order to obtain one set of

model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagrams, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner. A small set of model parameters is obtained. This is ideal for computer storage and calculation of properties and phase diagrams.

In previous publications, we reported complete critical reviews and thermodynamic optimizations of the ternary sub-systems CaO–Al₂O₃–SiO₂,²⁾ MnO–Al₂O₃–SiO₂,³⁾ CaO–MnO–SiO₂,⁴⁾ and CaO–MnO–Al₂O₃.⁴⁾ In the present article, only the optimized model parameters for the ternary sub-systems are used to predict the thermodynamic properties of the phases of the 4-component system using recently developed^{5,6)} approximation methods. No additional model parameters are required. Phase equilibrium diagrams are calculated from the predicted thermodynamic properties.

All available thermodynamic and phase equilibrium data at 1 bar total pressure for the quaternary system are critically reviewed. Agreement with the model predictions are shown to be, in general, within the experimental error limits. Not only equilibria among solid and liquid oxide phases

es, but also equilibria between liquid slags and manganese alloys, were considered.

In a few cases, there was disagreement between reported and calculated liquidus compositions. A few key experiments were thus carried out as part of the present study in order to resolve this conflict. It was found that the results verified the model calculations.

The thermodynamically consistent phase diagram sections, calculated from the model parameters, elucidate the complex phase relationships in this system, and phase equilibria are predicted in regions of temperature and composition where no measurements have been reported.

All thermodynamic calculations were performed with the FactSage thermodynamic computing system.¹⁾ Phase equilibria are calculated by global Gibbs energy minimization. By coupling the presently developed database with other evaluated F*A*C*T databases for metallic solutions, gases, *etc.*, FactSage can be used to compute complex slag/metal/solid/gas equilibria. For example, equilibrium between CaO–MnO–SiO₂–Al₂O₃ inclusions and alloy phases can be simulated and studied. Examples of applications to inclusion engineering of Mn/Si deoxidized steel will be presented elsewhere.⁷⁾

2. Thermodynamic Models

The thermodynamic properties and phase equilibria of all binary and ternary sub-systems of the CaO–MnO–Al₂O₃–SiO₂ quaternary system have been critically evaluat-

ed by the authors,^{2–4,8,9)} and optimized model parameters have been obtained which reproduce all available binary and ternary data within error limits.

The following solution phases (phases of variable composition) are found in the CaO–MnO–Al₂O₃–SiO₂ quaternary system^{2–4,8,9)}: (i) slag (molten oxide phase), CaO–MnO–AlO_{1.5}–SiO₂; (ii) olivine, (Ca, Mn)₂[Ca, Mn]₂SiO₄ (extending from γ -dicalcium silicate, Ca₂SiO₄, to tephroite, Mn₂SiO₄); (iii) monoxide s.s., CaO–MnO; (iv) wollastonite s.s., (Ca, Mn)SiO₃ (extending from wollastonite, CaSiO₃); (v) rhodonite s.s., (Mn, Ca)SiO₃ (extending from rhodonite, MnSiO₃); (vi) α -Ca₂SiO₄ s.s., (Ca, Mn)₂SiO₄ (extending from α' -dicalcium silicate, α' -Ca₂SiO₄); (vii) α' -Ca₂SiO₄ s.s., (Ca, Mn)₂SiO₄ (extending from α' -dicalcium silicate, α' -Ca₂SiO₄); (viii) mullite s.s.: non-stoichiometric “Al₆Si₂O₁₃”. As well, the following nearly stoichiometric compounds are found^{2–4,8,9)}: corundum (Al₂O₃), quartz (SiO₂), tridymite (SiO₂), cristobalite (SiO₂), Ca₃Al₂O₆, CaAl₂O₄, CaAl₄O₇, CaAl₁₂O₁₉, hartrurite (Ca₃SiO₅), rankinite (Ca₃Si₂O₇), galaxite (MnAl₂O₄), anorthite (CaAl₂Si₂O₈), gehlenite (Ca₂Al₂SiO₇), Mn-cordierite (Mn₂Al₄Si₅O₁₈) and spessartite (Mn₃Al₂Si₃O₁₂).

Liquidus projections of the four ternary sub-systems, calculated from the previously optimized model parameters, are shown in Fig. 1.

For the molten oxide (slag) phase, the Modified Quasichemical Model^{10,11)} was used. This model has been recently further developed and summarized.^{12,13)} This model takes into account short-range-ordering by consider-

Fig. 1. Liquidus surfaces of the four ternary subsystems of the CaO–MnO–SiO₂–Al₂O₃ system calculated from the thermodynamic models (temperature in °C).

Table 1. Experimental results for phase equilibria in the CaO–MnO–SiO₂–Al₂O₃ system.

No.	Temperature (°C)	Phases in Equilibrium†	Phase†	Weight %					Mole %			
				Al ₂ O ₃	MnO	CaO	SiO ₂	Al ₂ O ₃ /SiO ₂	Al ₂ O ₃	MnO	CaO	SiO ₂
1	1300	L	L	14.86	19.54	31.80	33.81	0.44	9.40	17.76	36.56	36.28
2	1300	L	L	15.55	13.73	34.45	36.27	0.43	9.75	12.38	39.27	38.60
3	1300	L + CAS2	L	20.14	12.63	22.06	45.17	0.45	12.99	11.71	25.87	49.43
			CAS2	37.93	0.64	17.72	43.71	-	26.12	0.63	22.19	51.06
4	1300	L	L	16.06	23.02	25.72	35.20	0.46	10.32	21.26	30.05	38.38
5	1300	L	L	17.16	16.11	29.06	37.67	0.46	10.92	14.75	33.63	40.70
6	1300	L	L	14.89	25.58	26.93	32.60	0.46	9.55	23.58	31.40	35.48
			L	13.04	8.52	39.99	38.45	0.34	7.99	7.50	44.54	39.97
7	1300	L+C2AS	C2AS	35.49	1.53	38.09	24.88	-	23.79	1.47	46.43	28.31
			L	16.48	28.70	8.45	46.38	0.36	10.85	27.18	10.12	51.85
8	1200	L+CAS2	CAS2	37.05	1.00	18.19	43.76	-	25.41	0.99	22.68	50.92
			L	15.71	26.19	17.58	40.51	0.39	10.20	24.43	20.75	44.62
9	1200	L+CAS2	CAS2	38.52	0.55	16.82	44.12	-	26.61	0.54	21.12	51.72
			L	15.71	26.19	17.58	40.51	0.39	10.20	24.43	20.75	44.62

† Notations L, CAS2 and C2AS are used for the liquid phase, anorthite (CaAl₂Si₂O₈) and gehlenite (Ca₂Al₂SiO₇), respectively.

ing second-nearest-neighbor pair exchange reactions. Although manganese can exist in liquid slags in the trivalent state at high oxygen partial pressures, the present study is limited to relatively reducing conditions where only divalent manganese is present in appreciable amounts.

The thermodynamic properties of the quaternary liquid solution were estimated solely from the optimized binary and ternary model parameters, using the approximation methods recently developed by Chartrand and Pelton⁵⁾ and Pelton.⁶⁾ The importance of correctly selecting an “asymmetric (Toop-like)” or “symmetric (Kohler-like)” approximation for each ternary system has been discussed^{5,6)} and has been recently demonstrated⁴⁾ for the case of the CaO–MnO–Al₂O₃ system. The new approximation method for multicomponent systems permits a free choice of the appropriate approximation method for each ternary subsystem, and permits these to be properly combined to estimate the properties of a multicomponent solution.

No additional model parameters were added in the present study.

The Gibbs energy of the olivine solid solution was modeled using the Compound Energy Formalism,¹⁴⁾ taking the two cationic sub-lattices into account. Other solid solutions such as monoxide s.s., wollastonite s.s., rhodonite s.s., and α - and α' -Ca₂SiO₄ s.s. were modeled by polynomial expansions of the excess Gibbs energies. The nonstoichiometry of mullite s.s. was described by a general defect model⁹⁾ similar to the Wagner–Shottky model.¹⁵⁾ No changes were made to the previously optimized^{2–4,8,9)} model parameters.

It was assumed that there is no solubility of the fourth component in any solid phase previously modeled in a ternary sub-system. That is, MnO is assumed to be insoluble in all solid phases of the CaO–Al₂O₃–SiO₂ system, *etc.*, and it was assumed that there are no quaternary compounds.

3. Experimental

Several equilibrium measurements were performed to verify the thermodynamic modeling of the quaternary system. Oxide mixtures were equilibrated at high temperatures at saturation with metallic Mn, and were quenched rapidly in ice-water. The equilibrium phase compositions were subsequently analyzed by electron probe microanalysis (EPMA).

Oxide powders of MnO (99.9 mass%, supplied by

Fig. 2. Electron image (back scattered): L=liquid, A=anorthite (CaAl₂Si₂O₈) and M=metallic Mn.

Fig. 3. Electron image (back scattered): L=liquid, G=gehlenite (Ca₂Al₂SiO₇) and M=metallic Mn.

Kosundo) and SiO₂ (99.9 mass%, supplied by Kosundo), Al₂O₃ (99 mass%, supplied by Kanto) and CaO calcined from CaCO₃ (99.5 mass%, supplied by Kanto) were used as starting materials. The pure powders were dried at 100°C, weighed in the desired proportions and mixed with metallic Mn (99.99 mass%, supplied by Alfa) thoroughly in an agate mortar. The mixtures were pelletized and placed in a molybdenum envelope (99.5 mass%). The molybdenum envelope was placed in a graphite holder in a fused alumina reaction tube, and the assemblage was equilibrated at the

desired temperature under an atmosphere of Ar gas, purified by passing over $\text{Mg}(\text{ClO}_4)_2$ and Mg chips at 450°C.

At the beginning, the temperature was set approximately 100°C higher than the final temperature of equilibration in order to promote homogenization of the sample. After 1 h, the temperature was decreased to the desired equilibration temperature. The temperature was measured with a Pt-6%Rh/Pt-30%Rh thermocouple located adjacent to the sample. After equilibration for 40 to 60 h, the assemblage was removed from the furnace and quickly quenched in ice-water.

Quenched samples were mounted and polished. Microstructures were observed by optical microscopy as well as by SEM, and the compositions of the phases were measured by EPMA (JEOL JXA-8100), using an accelerating voltage of 15 kV and a probe current of 40 nA. CaWO_4 , SiO_2 , MnO and Al_2O_3 were used as standards for the EPMA measurements of the calcium, silicon, manganese and aluminum concentrations, respectively. Since the oxygen concentration is not directly measured by EPMA, the composition in terms of the oxide components was calculated from their stoichiometries (assuming all Mn as MnO). The ZAF correction procedure was applied. The average accuracy of the EPMA measurements was within 1 wt%.

The experimental results are summarized in Table 1. Figures 2 and 3 show typical back-scattered pictures of the quenched samples.

4. Comparison of Model Predictions with Experimental Data

4.1. Activity of MnO

Abraham *et al.*¹⁶⁾ measured the activity of MnO in $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MnO}$ (<10 wt%) liquid slags using a slag/gas/Pt equilibration technique at 1 650°C under reducing conditions. Similarly, Morita *et al.*¹⁷⁾ determined the activity of MnO using a slag/gas/Cu equilibration at 1 600°C. Recently, Donato and Granati¹⁸⁾ measured the activity of MnO at MnO concentrations up to 15 wt% in lime-saturated low-silica slags at 1 600°C using a slag/gas/Pt equilibra-

tion technique.

Figure 4 compares the activities of MnO predicted from the present study with the experimental data. The agreement is within experimental error limits except for line K. However, compositions along lines K and C are very similar, and the predictions and experiments are in reasonable agreement for line C. Several authors^{17,19-21)} also measured the Henrian activity coefficients of MnO in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ slags using slag/metal equilibration techniques at temperatures between 1 500°C and 1 650°C. However, these results are quite scattered and in disagreement with each other and with experimental data shown in Fig. 4 at low MnO contents.

Several years ago, Li *et al.*²²⁾ reported that activities of MnO in $\text{CaO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ slags, calculated from the F*A*C*T database,¹⁾ were lower than the experimental data. The F*A*C*T database at the time was in error due to an erroneous optimization of the $\text{MnO-Al}_2\text{O}_3$ binary system²³⁾ which employed incorrect²⁴⁾ values for the Gibbs energy of MnAl_2O_4 , resulting in an overestimation of the stability of $\text{MnO-Al}_2\text{O}_3$ melts. This situation has now been remedied by a new optimization³⁾ of the $\text{MnO-Al}_2\text{O}_3$ system and, as shown in the present study, MnO activities are now correctly predicted by the model.

4.2. Phase Diagrams of the $\text{CaO-MnO-SiO}_2\text{-Al}_2\text{O}_3$ System

Rait and Olsen²⁵⁾ measured the liquidus of the $\text{CaO-MnO-Al}_2\text{O}_3\text{-SiO}_2$ system at $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratios of 0.25 and 0.5 at 1 450°C, 1 500°C and 1 550°C under Ar atmospheres. The compositions of the liquid slag in quenched samples were determined by EPMA. Recently, using the same technique, Roghani *et al.*^{26,27)} reported phase equilibrium studies at $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratios of 0.41, 0.55 and 0.65 at temperatures between 1 100°C and 1 450°C. As well, there are the results of the present experiments (Table 1).

In Fig. 5, the calculated liquidus surface of the monoxide phase at $\text{Al}_2\text{O}_3/\text{SiO}_2$ weight ratios of 0.25 and 0.5 at 1 450°C, 1 500°C and 1 550°C is compared with the experimental data of Rait and Olsen.²⁵⁾ The agreement is very

Fig. 4. Calculated activities of MnO in $\text{CaO-MnO-SiO}_2\text{-Al}_2\text{O}_3$ liquid slags (with respect to the pure solid standard state).

(a)

(b)

Fig. 5. Calculated liquidus surface of the CaO-MnO-SiO₂-Al₂O₃ system at 1450°C, 1500°C and 1550°C at Al₂O₃/SiO₂ weight ratios of (a) 0.25 and (b) 0.5.

good. It is noteworthy that the positions of the liquidus curves in Figs. 5(a) and 5(b) are nearly the same.

The calculated liquidus surface at an Al₂O₃/SiO₂ weight ratio of 0.41 at 1200°C and 1300°C is plotted in Fig. 6 along with the three anorthite liquidus points from Table 1 (No. 3, 8, 9), and with a gehlenite liquidus point from Table 1 (No. 7) for which the Al₂O₃/SiO₂ ratio is approximately 0.41 (0.34–0.46). Experimental liquidus points from Roghani *et al.*,²⁶⁾ for which the Al₂O₃/SiO₂ ratio is also approximately 0.41 (0.39–0.46), are also plotted in Fig. 6. Finally, the five composition points from the present study (Table 1) at which only a single liquid phase was observed at these temperatures are also plotted. It can be seen that the calculations are in good agreement with the present experi-

Fig. 7. Experimentally determined compositions of gehlenite (Ca₂Al₂SiO₇) and anorthite (CaAl₂Si₂O₈) in equilibrium with liquid. Symbols: ○ and + represent gehlenite and anorthite, respectively, according to the report by Roghani *et al.*^{26,27)}; □ and ◇ represent gehlenite and anorthite, respectively, from the present study.

Fig. 6. Calculated liquidus surface of the CaO-MnO-SiO₂-Al₂O₃ system at an Al₂O₃/SiO₂ weight ratio of 0.41 at 1200°C and 1300°C. Dashed line is the liquidus proposed by Roghani *et al.*²⁶⁾ Experimental points from Roghani *et al.*²⁶⁾ and from the present study were measured at Al₂O₃/SiO₂ weight ratios over the range 0.34 to 0.46.

Fig. 8. Predicted liquidus surface of the CaO-MnO-SiO₂-Al₂O₃ system at 15 wt% Al₂O₃.

Fig. 9. Predicted liquidus surface of the CaO-MnO-SiO₂-Al₂O₃ system at 30 wt% CaO.

mental points, but are in agreement with the points of Roghani *et al.*²⁶⁾ only for the monoxide liquidus. Note that the measured MnO contents of the anorthite and gehlenite phases are all below 1.5 wt%, thereby confirming the assumption of negligible solubility used in the calculations.

Roghani *et al.*^{26,27)} reported compositions of gehlenite in equilibrium with the liquid which deviate significantly from the stoichiometric composition, whereas in the present study the measured compositions were much closer to stoichiometric Ca₂SiAl₂O₇, as shown in Fig. 7. The gehlenite grains in the experiments of Roghani *et al.*²⁶⁾ were smaller than 10 μm in diameter, whereas in the present study the grains were larger than 100 μm with well-formed facets.

Possibly, full equilibrium was not achieved in the experiments of Roghani *et al.*,^{26,27)} thereby explaining the discrepancy in the gehlenite liquidus in Fig. 6. For anorthite, however, the solid compositions reported by these authors did correspond closely to the stoichiometric composition (Fig. 7), so the discrepancy in Fig. 6 regarding the anorthite liquidus remains unexplained.

Agreement between the present calculations and phase diagrams reported by Roghani *et al.*²⁷⁾ at other Al₂O₃/SiO₂ ratios is generally similar to that in Fig. 6. Several calculated (predicted) liquidus projections of importance to steel-making (Figs. 8 and 9) and manganese alloy production (Fig. 10) are shown in Figs. 8 to 10. Figures 8 and 9 show

Fig. 10. Predicted liquidus temperature of the CaO-MnO-SiO₂-Al₂O₃ system at 5 and 10 wt% MnO, for Al₂O₃/SiO₂ weight ratios of (a) 0.5, (b) 1, (c) 2 and (d) 3.

the liquidus surface of the CaO-MnO-SiO₂-Al₂O₃ system at 15 wt% Al₂O₃ and 30 wt% CaO respectively. These figures can be used to estimate the precipitation temperature and phase compositions of inclusions in Mn/Si deoxidized steel which may react with CaO-SiO₂ type top slags during the production of semi-killed steel. Figure 10 shows the liquidus temperature of the CaO-MnO-SiO₂-Al₂O₃ system at low MnO contents, for different CaO/Al₂O₃ weight ratios. This result is of interest to manganese alloy production.

Calculated iso-activity lines of MnO and SiO₂ in quaternary slags at 1550°C are shown in Fig. 11.

4.3. Slag/Alloy Equilibria

Ding and Olsen²⁸⁾ studied the equilibrium between CaO-MnO-Al₂O₃-SiO₂ slags and C-saturated or SiC-saturated Mn-Si-C alloys held in a graphite crucible. After equilibration and quenching, the compositions of the slag and metal phases were determined by EPMA and chemical analysis respectively. Their results are compared in Fig. 12 with the model calculations which are presented as curves showing the slag compositions in equilibrium with Mn-Si-C alloys of constant weight percent Si. The agreement is good. In the calculations, the thermodynamic properties of the alloys were calculated using the optimized database of Tang and Olsen.²⁹⁾

Ding and Olsen³⁰⁾ performed similar measurements at 1500°C, using C-saturated Mn-Fe-Si-C alloys containing

11 wt% Fe, and fixing the CO partial pressure at 1.0 atm. These results are plotted in Fig. 13 where it can be seen that agreement with the calculations is very good. In the calculations, the entire F*A*C*T¹⁾ database for the slag phase, including FeO as a component, was used. The calculated FeO content, however, was less than 0.01 wt%.

5. Conclusions

A complete literature review, critical evaluation, and thermodynamic modeling of phase diagrams and thermodynamic properties of the CaO-MnO-Al₂O₃-SiO₂ system at 1 bar pressure have been carried out. The resultant database of optimized model parameters can be used to calculate all thermodynamic properties and any phase diagram section using the FactSage¹⁾ thermochemical system.

Only previously optimized parameters for the four ternary subsystems were required in order to reproduce (*i.e.* predict) all available quaternary data, including metal/slag equilibrium data, within experimental error limits. This lends strong support to the models which were used, and to the recently developed^{5,6)} approximation techniques. It also gives credence to phase equilibria calculated in regions of composition and temperature where no measurements have been reported.

In the few cases where there was disagreement between measured and calculated quaternary liquidus temperatures,

Fig. 11. Predicted iso-activity lines of MnO and SiO₂ (with respect to the pure solid standard states) in CaO-MnO-SiO₂-Al₂O₃ liquid slags at 1550°C (a) at constant Al₂O₃/SiO₂ weight ratio of 1.5 and (b) at constant 15 wt% Al₂O₃.

Fig. 12. Calculated composition of CaO-MnO-SiO₂-Al₂O₃ liquid slag with Al₂O₃/SiO₂ weight ratios of (a) 1.5 and (b) 3.0 in equilibrium with C-saturated or SiC-saturated Mn-Si-C alloys of indicated constant weight percent of Si at 1550°C.

Fig. 13. Calculated composition of CaO-MnO-SiO₂-Al₂O₃-(FeO) liquid slag with a Al₂O₃/SiO₂ weight ratio of 1.5 in equilibrium with C-saturated Mn-11wt%Fe-Si-C alloys of indicated constant weight percent Si at 1550°C. Dashed line is the calculated composition of the liquid slag in equilibrium with the manganese alloy and a gas phase with $P_{\text{CO}} = 1$ atm. Experimental points (solid circles) of Ding and Olsen³⁰ at $P_{\text{CO}} = 1$ atm are also shown. The calculated FeO content of the slag is less than 0.01 wt%.

new measurements performed as part of the present study have verified the calculations.

By coupling the presently developed database with other evaluated $F^*A^*C^*T^{(1)}$ databases for metallic solutions, gases, etc., complex slag/metal/solid/gas equilibria can be computed. In a subsequent article⁷⁾ the reliability of these calculations as applied to inclusion engineering in Mn/Si deoxidized steel will be demonstrated.

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