

Development of NiO-CaO-MgO-SiO₂ thermodynamic database using experimental and thermodynamic modelling approaches with focus on NiO-MgO-SiO₂ and NiO-CaO-SiO₂ systems

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Abstract: An integrated research program is under way to develop a thermodynamic database for the Al₂O₃-CaO-FeO-Fe₂O₃-NiO-MgO-SiO₂ chemical system. The program incorporates experimental and thermodynamic modelling studies. The NiO-MgO-SiO₂ and NiO-CaO-SiO₂ systems were experimentally investigated and reported and a thermodynamic database for the NiO-CaO-MgO-SiO₂ system was developed.

High-temperature equilibration and rapid quenching techniques were used to study the phase equilibria in the NiO-MgO-SiO₂ and NiO-CaO-SiO₂ systems in air. The compositions of phases were measured accurately using electron probe X-ray microanalysis (EPMA). Selected experiments were carried out to resolve discrepancies in the available literature data.

Computerized thermodynamic databases for the liquid slag and solid oxide phases in the NiO-CaO-MgO-SiO₂ system were developed by critical evaluation/optimization of all available phase equilibrium and thermodynamic data. The Modified Quasichemical Model was used for the slag (molten oxide) phase. The models based on the Compound Energy Formalism were developed for the olivine, spinel and pyroxene solid solutions.

Keywords: Phase equilibrium, Thermodynamic modelling

1. Introduction

The production of nickel from Ni Laterite ores containing both Limonite (mainly Fe hydro-oxide) and Saprolite (mainly Mg hydrosilicate) is increasing. Nickel Saprolite ores, which contain high concentrations of magnesium and silicon, are often processed by high temperature smelting to produce ferronickel alloy. The chemistry of the smelting processes can be represented by the Al_2O_3 -CaO-FeO- Fe_2O_3 -MgO-NiO- SiO_2 system. Despite the importance of this multi-component system, the phase equilibria and thermodynamics are not well described, even in the lower order sub-systems. A reliable characterisation of this system is necessary to optimise the control of bath fluxing and operating temperatures, improve Ni extraction, reduce operating costs and support the development of novel commercial pyrometallurgical extraction processes. The experimental difficulties associated with high temperature equilibration of these systems appear to be the principal reason for lack of information on phase equilibria and thermodynamic properties of phases in this system.

In the present study, a combination of thermodynamic modelling and experimental studies is used to characterise NiO-containing multi-component oxide systems at high temperature of interest to nickel pyrometallurgical processes. It is part of an on-going research program to develop a self-consistent multi-component thermodynamic database. This approach has enabled the characterisation of phase relations over the wide range of compositions, temperatures and oxygen pressures of importance to metallurgical and power generation industries.

2. Research methodology

2.1 Experimental method

The experimental technique used involved the preparation of an oxide mixture sample of predetermined composition. The sample was equilibrated at a fixed temperature in air and quenched. On rapid cooling the liquid phase converts to glass so that the phase assemblage which exists at high temperature is "frozen in". The compositions of the solid and liquid phases were then measured by electron probe X-ray microanalysis (EPMA).

A. Preparation of oxide mixtures

The starting mixtures were made from CaO (99.98 wt% purity), NiO (99.99 wt% purity), MgO (99.99 wt% purity) and SiO_2 (99.98 wt% purity) supplied by Sigma-Aldrich Co. Mixtures of selected bulk compositions were prepared by weighing the high purity powders and mixing them thoroughly using an agate mortar and pestle. The initial compositions of the mixtures were selected in such a way that a liquid phase was in equilibrium with one or more solid phases. Each mixture was then compacted with pressure of 40 MPa to produce a pellet weighing less than 0.2 gram. 10 mm x 12 mm envelopes made from 0.025 mm-thick platinum foil supplied by AGR Metthey (Melbourne, Australia) were used as sample containers. It was found that platinum is inert to the sample materials under the investigated conditions so there is no contamination of the samples.

B. High temperature equilibration technique

All equilibration experiments were conducted in a vertical reaction tube (impervious re-crystallized alumina, 30-mm i.d.) in electrical resistance heated furnaces with silicon carbide (SiC) elements. The sample was introduced from the bottom of the vertical tube furnace and suspended by a sample holder constructed using Pt wire. The 30-mm i.d. re-crystallized alumina reaction tube was preconditioned at the target temperature for more than 5 minutes, and the specimen was then raised into the uniform temperature hot zone of the furnace.

Pre-melting of the sample was carried out by increasing the temperature 25 °C above the target temperature. Pre-melting ensured that samples were homogenised, and the fresh solid phases precipitated rather than undissolved solids were left. After 30 minutes of pre-melting, the temperature of the furnace was decreased back to the target temperature and the sample was equilibrated inside the furnace for at least 24 hours.

After the equilibration, the specimen was rapidly quenched by dropping it directly into the iced water. The quenched sample was dried on a hot plate, crushed into smaller pieces, which were mounted in epoxy resin, polished using conventional metallographic polishing techniques and carbon coated for subsequent electron probe X-ray microanalysis (EPMA).

C. Control of temperature

To monitor the actual temperature surrounding the sample, a working thermocouple was placed in a re-crystallised alumina thermocouple sheath immediately adjacent to the sample. The working thermocouple was calibrated against a standard thermocouple (supplied by the National Measurement Institute of Australia, NSW, Australia). The temperature of the experiment was continuously controlled within ± 1 °C of the target temperature. It is estimated that the overall absolute temperature accuracy of the experiment is within 5 °C.

D. Analysis technique

The rapid quenching technique successfully retains the liquid slag as a homogenous glassy phase. The compositions of various phases were measured using JEOL 8200L EPMA with wavelength dispersive detectors (JEOL is a trademark of Japan Electron Optics Ltd., Tokyo). A 15-kV accelerating voltage and 15 nA probe current were selected for the micro-analyzer operation. The standards (Charles M. Taylor, Stanford, CA) used in the EPMA measurements were as follows: wollastonite (CaSiO₃) for Ca and Si, magnesite (MgO) for Mg and Ni olivine (Ni₂SiO₄) for Ni. The Duncumb–Philibert correction based on atomic number, absorption, and fluorescence (ZAF correction, supplied by JEOL) was applied. The compositions were measured with an accuracy of 1 wt %. Only the Me-cations concentrations were measured with EPMA; the corresponding oxidation states were assigned.

E. Assessment of achievement of equilibrium

Particular attention was paid to achievement of equilibrium that was continuously re-confirmed by i) equilibration at different times, ii) checking the uniformity of phase compositions across the samples, iii) approaching equilibrium from different directions and iv) considering possible reactions taking place in the sample during equilibration.

Selected experiments were carried out at different times in order to determine the minimum time required to attain equilibrium; for example, Table 1 reports results of experiments with a sample of the Ni-Mg-Si-O system equilibrated for 12, 24, 36 and 48 hours.

Table 1 Measured phase compositions for sample equilibrated at different times

Time of equilibration /hours	Temperature	Log ₁₀ [P(O ₂), atm]	Phase at equilibrium	Composition Mol%		
	°C			SiO ₂	NiO	MgO
12	1570 °C	-0.6778 (Air)	Liquid	54.1	16.0	29.9
			Cristobalite	99.9	0.1	0.0
24			Liquid	59.5	12.1	28.4
			Cristobalite	99.7	0.3	0.0
36			Liquid	59.1	12.2	28.7
			Cristobalite	99.6	0.4	0.0
48			Liquid	59.6	11.9	28.5
			Cristobalite	99.6	0.4	0.0

The SiO₂ concentration in the liquid phase remains constant within the measurement uncertainty for equilibration times of 24 hours or greater. The minimum time for equilibration of 24 hours was selected.

The uniformity of phase compositions across the sample was checked by EPMA. Six sampling points were selected for each phase. The samples were re-crushed and re-equilibrated if variations within one single phase were found to be greater than 1%wt. Traces of incomplete reactions were searched in all samples to ensure the phases in the final results correspond to the equilibrium.

2.2 Thermodynamic modelling

The thermodynamic modelling has been carried out using the FactSage thermochemical software and its databases [1]. Thermodynamic databases are developed through thermodynamic optimization that involves selection of proper thermodynamic models for all phases in a system, critical simultaneous evaluation of all available thermodynamic and

phase equilibrium data and optimization of thermodynamic model parameters to obtain one self-consistent set of model equations for the Gibbs energies of all phases best reproducing the experimental data as functions of temperature and composition (the information repeated). From these equations, the thermodynamic properties and the phase diagrams can be back-calculated. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be identified during the development of the model. These discrepancies can then be resolved through new experimental studies that, if possible, are undertaken in areas essential for further thermodynamic optimizations. Multi-component data, if available, are used to derive low-order (binary and ternary) model parameters, and if multi-component data for a system are lacking, the low-order parameters are extrapolated. In this way, the thermodynamic databases are developed and all the data are rendered self-consistent and consistent with thermodynamic principles.

The molten slag phase is modelled using the Modified Quasichemical Model [2–3] in which short-range-ordering is taken into account. Solid solutions are mainly modelled in the framework of the Compound Energy Formalism [4], taking into account the crystal structure and physical nature of each solution. Some other solution phases were optimized earlier [5]. They are wollastonite, α -Ca₂SiO₄ and α' -Ca₂SiO₄.

Solution phases in the CaO-MgO-NiO-SiO₂ quaternary system were modeled as described below. Phase names with the corresponding formulas and notations are all given in Table 2. Cations shown within a set of parentheses occupy the same sublattice.

Table 2 All solution phases and stoichiometric compounds found in the CaO-MgO-NiO-SiO₂ system

Phase name	Formula	Notations
Solution phases:		
Slag (liquid oxide phase)	CaO-MgO-NiO-SiO ₂	L or Liquid
Monoxide (solid oxide phase)	CaO-MgO-NiO	Monoxide
Olivine	(Ca ²⁺ , Mg ²⁺ , Ni ²⁺) ^{M2} (Ca ²⁺ , Mg ²⁺ , Ni ²⁺) ^{M1} SiO ₄	Olivine
Clino-pyroxene (<i>C2/c</i> , monoclinic)	(Ca ²⁺ , Mg ²⁺ , Ni ²⁺) ^{M2} (Mg ²⁺ , Ni ²⁺) ^{M1} Si ₂ O ₆	cpx
Proto-pyroxene (<i>Pbcn</i> , orthorhombic)	(Ca ²⁺ , Mg ²⁺ , Ni ²⁺) ^{M2} (Mg ²⁺ , Ni ²⁺) ^{M1} Si ₂ O ₆	ppx
Wollastonite	(Ca ²⁺ , Mg ²⁺)SiO ₃	woll
α -Ca ₂ SiO ₄	(Ca ²⁺ , Mg ²⁺) ₂ SiO ₄	a-Ca ₂ SiO ₄
α' -Ca ₂ SiO ₄	(Ca ²⁺ , Mg ²⁺) ₂ SiO ₄	a'-Ca ₂ SiO ₄
Stoichiometric compounds:		
Akermanite	Ca ₂ MgSi ₂ O ₇	
Merwinite	Ca ₃ MgSi ₂ O ₈	
Pseudo-wollastonite	CaSiO ₃	p-woll
Hatrumite	Ca ₃ SiO ₅	
Rankinite	Ca ₃ Si ₂ O ₇	
Silica (quartz, tridymite, cristobalite)	SiO ₂	qz, trid, crist

3. Results and discussion

3.1 CaO-NiO-SiO₂

Phase equilibria in the CaO-NiO-SiO₂ system were studied by several authors [6-8] using quenching technique followed by microscopic and X-ray diffraction phase analysis at temperatures from 1100 °C to 1550 °C.

Although melting temperatures of niopside (CaNiSi₂O₆) obtained by Biggar [6] and Pretorius and Muan [7] are in agreement, they were considered questionable as they did not permit consistent optimizations. Therefore, a few critical experiments have been performed to determine solidus temperature on the CaSiO₃-NiSiO₃ section of the system. Some uncertainties were also found in the phase diagrams reported by Biggar [6]. Biggar [6] observed nickel orthosilicate above its melting temperature of 1545 °C. As an explanation, he suggested the existence of the crystalline solution of Ni₂SiO₄ containing small amount of Ca. However, no evidence for this result was found in literature. Furthermore, the two-phase region containing liquid and CaSiO₃, and the three-phase region containing liquid, CaSiO₃, and SiO₂ at 1390 °C determined by Biggar [6] were considered questionable since it was rather difficult to describe them in subsequent optimization. To resolve this issue, the CaO-NiO-SiO₂ ternary phase equilibria have been experimentally investigated.

Examples of typical microstructures of equilibrated samples are shown in Figure 1.

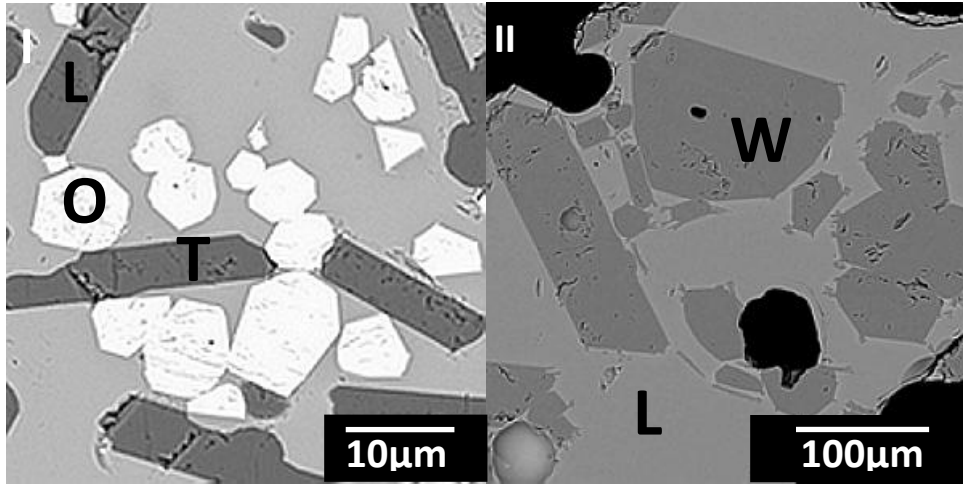


Figure 1 Backscattered SEM micrographs typical of equilibrated Ni-Ca-Si-O systems (I) Liquid (L), Olivine (O) and Tridymite (T) at 1643.15 K in air; (II) Liquid (L) and wollastonite (W) at 1673.15 K in air

The equilibrated phases were found to have good contact with each other and a dense structure was obtained which suggested a well equilibrated process. A homogenous glassy(liquid) phase was obtained indicating the liquid was well quenched; the composition of each phase measured by EPMA was found to be uniform. The experimental results and calculated phase diagram using thermodynamic databases developed in present study are plotted in Figures 2-4.

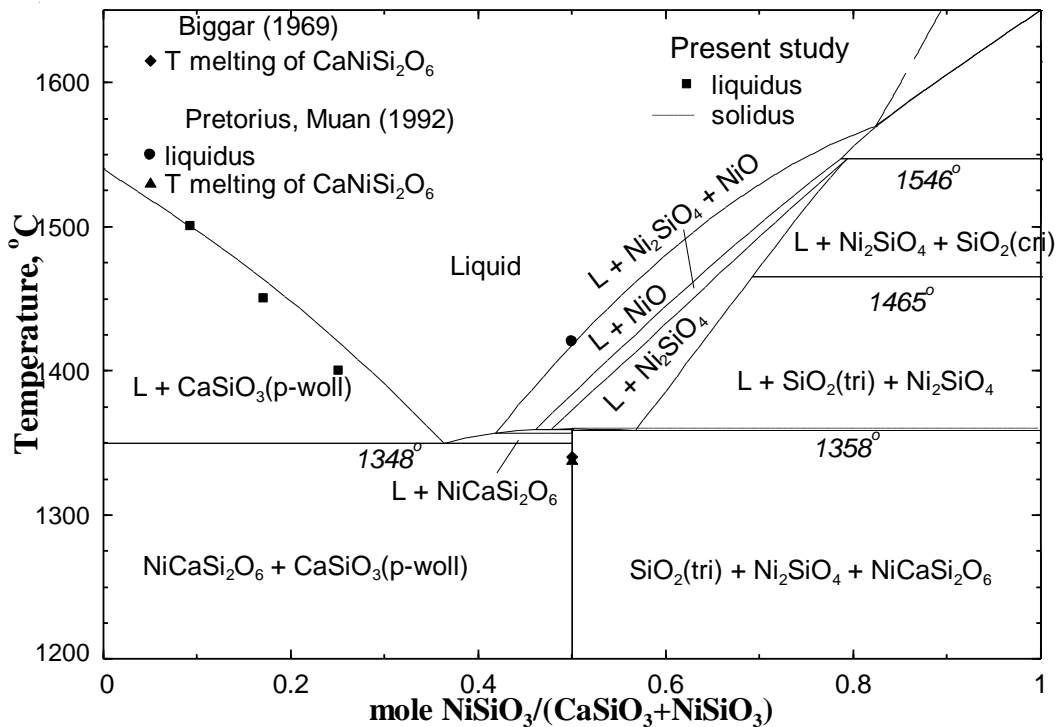


Figure 2 Calculated $\text{CaSiO}_3\text{-NiSiO}_3$ section of the CaO-NiO-SiO_2 system along with the literature data [6-7] and results of current experiments

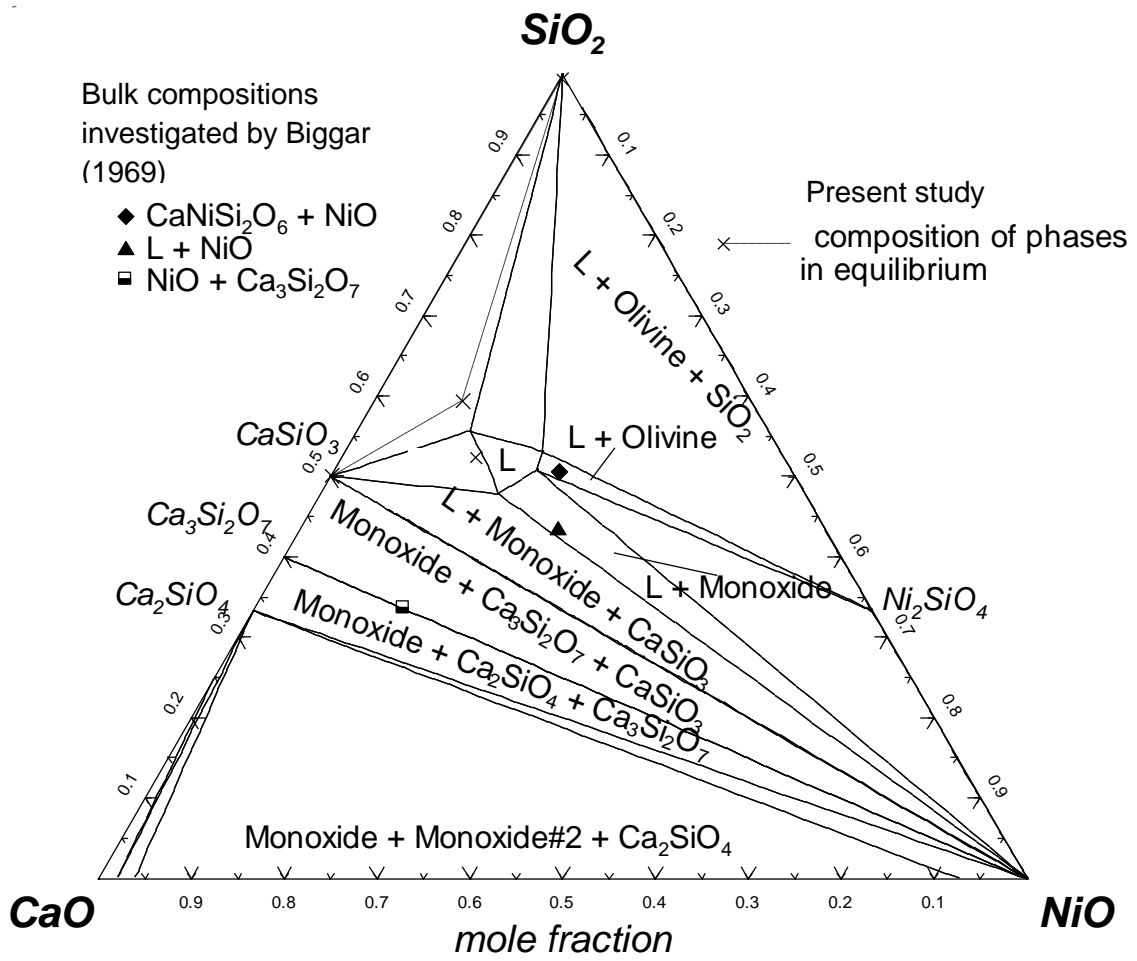


Figure 3 Calculated isothermal section of the CaO-NiO-SiO₂ system at 1360 °C along with the literature data of Biggar [6] and this study experimental results

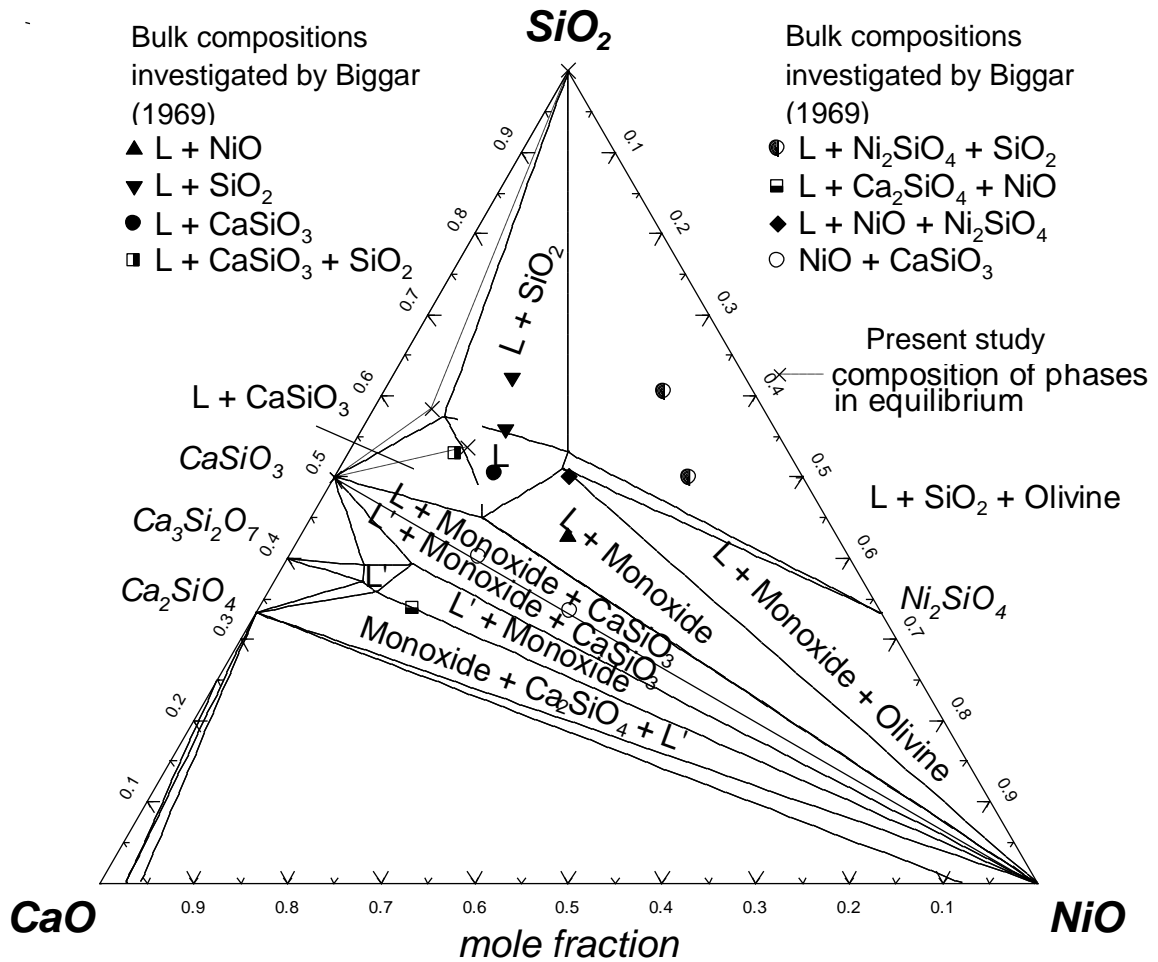


Figure 4 Calculated isothermal section of the CaO-NiO-SiO₂ system at 1390 °C along with the literature data of Biggar [6] and this study experimental results

As it can be seen from Figure 3, the predicted value of 1358 °C agrees well with the melting point of niopside (CaNiSi₂O₆) which was found in between 1350 °C to 1360 °C. The experimental results in the liquid-CaSiO₃ and liquid-SiO₂-CaSiO₃ regions indicated that the previously reported results of Biggar [6] were erroneous, therefore, they were not taken into consideration during optimisation; experimental results in the liquid-CaSiO₃ region were found to be well described using the revised model within experimental error limit; however, less SiO₂ in the liquid in the liquid-SiO₂-CaSiO₃ region at 1360 °C was predicted using the databases developed in present study.

3.2 MgO-NiO-SiO₂

Phase equilibria in the subsolidus region of the MgO-NiO-SiO₂ system, including those with proto-pyroxene ((Mg,Ni)SiO₃), were studied using quenching method followed by XRD and EPMA analysis in air between 927 °C and 1400 °C [9-12]. The maximum solubility of NiSiO₃ in the proto-pyroxene solution was found to be in the range of 9.6 mol% to 13 mol% at temperatures between 1100 °C and 1400 °C. The results obtained by Ottonello and Morlotti [13] question the existence of a continuous range of solid solutions between Mg₂SiO₄ and Ni₂SiO₄. Since there is no data on olivine/monoxide and olivine/proto-pyroxene equilibria at high temperatures (>1100 °C) in the literature, these were measured experimentally at 1400 °C and 1500 °C in the current study. The limit of existence of proto-pyroxene solution was also re-investigated in this study at the same temperatures to resolve inconsistency in the literature data.

Phase equilibria data including liquid are limited and some inconsistencies were found in the published literature. Ringwood [14] determined the phase diagram of the orthosilicate Mg₂SiO₄-Ni₂SiO₄ section using quenching technique

followed by an optical microscopic observation, the obtained data are in disagreement with other literature data in the limiting binary NiO-SiO₂ system with respect to a melting temperature of Ni₂SiO₄ olivine. Grutzeck and Muan [15] measured phase equilibria in the MgO-NiO-SiO₂ system by employing quenching technique with optical microscopy and X-ray diffraction. Their liquidus data are quite scattered. Therefore, phase equilibria in the liquidus region in the temperature range 1570-1650 °C were re-investigated in the present study.

Examples of typical microstructures of equilibrated samples are shown in Figure 5.

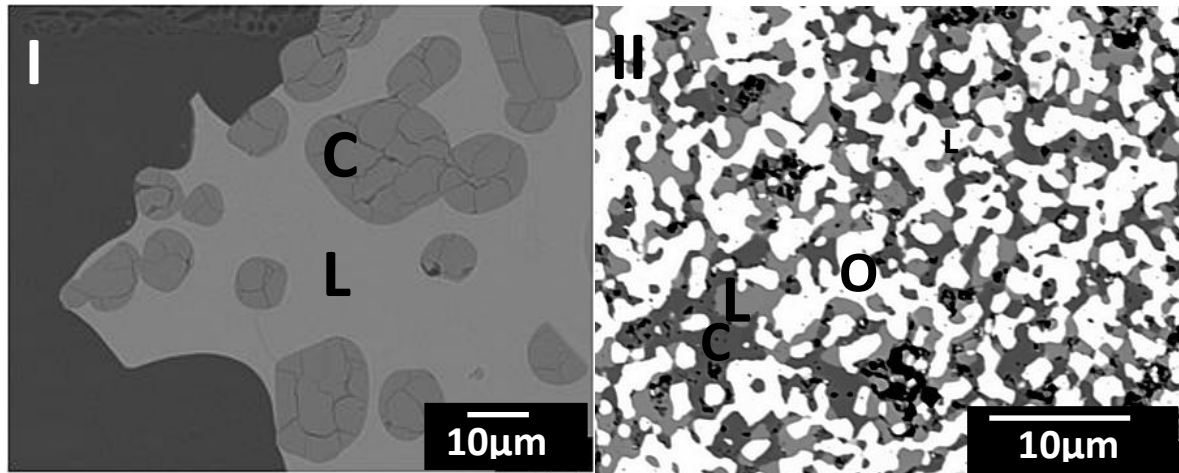


Figure 5 Backscattered SEM micrographs typical of equilibrated Ni-Mg-Si-O systems (I) Liquid (L) and Cristobalite (C) at 1643.15 K in air; (II) Liquid (L), Olivine (O) and Cristobalite (C) at 1673.15 K in air

As it can be seen from Figure 6, the results of the current study show there is a complete solid solution between Ni olivine and Mg olivine at 1400 °C; maximum solubility of NiSiO₃ in pyroxene solution was found to be 9.12 mol% at 1400 °C, lower than the result reported by Campbell and Roeder [9]. Tie lines in both olivine-monoxide and pyroxene-olivine regions determined in the present study were well described by databases developed in the present study

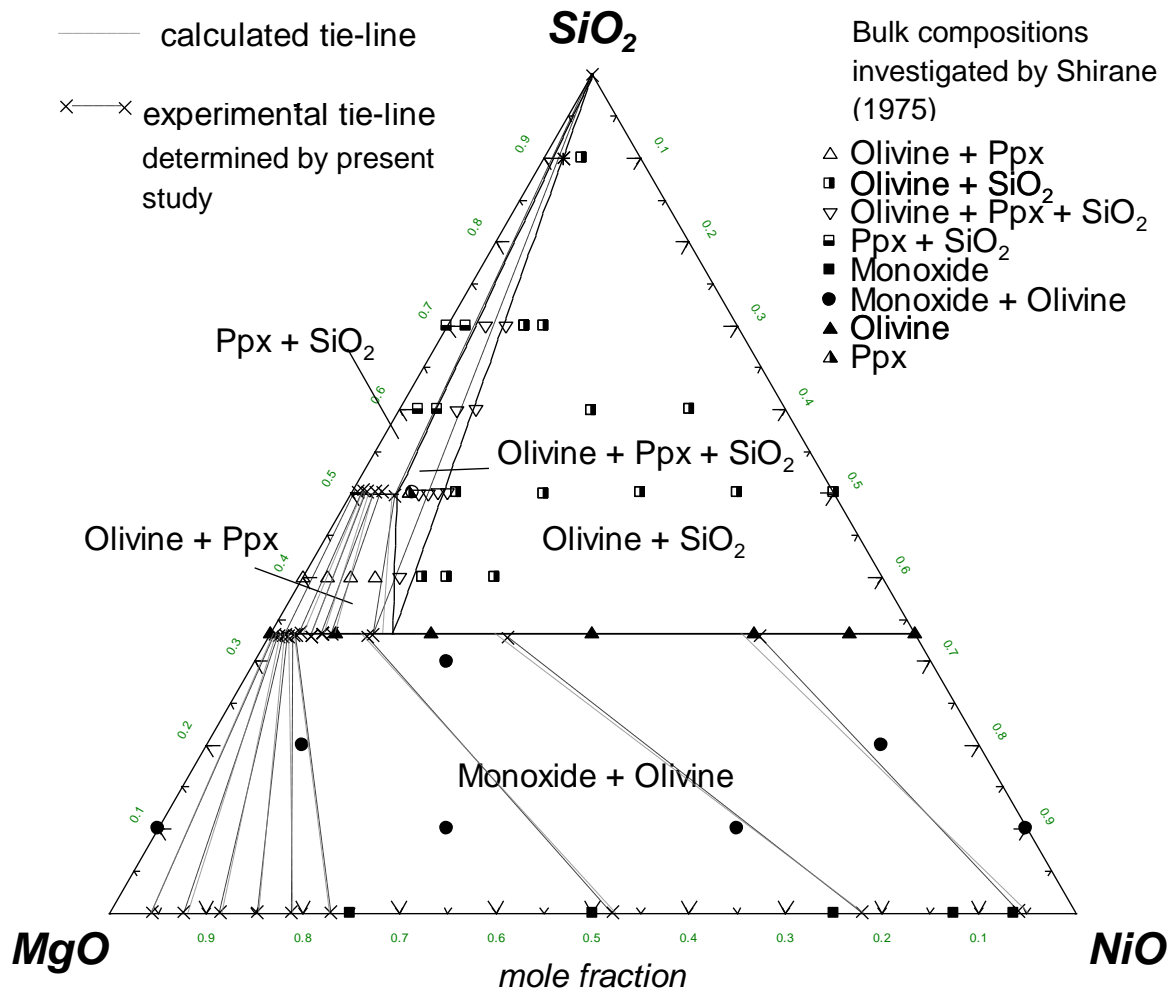


Figure 6 Isothermal section of the MgO-NiO-SiO₂ system at 1400 °C along with the calculated and experimental tie-lines measured in this study as well as experimental results [9, 12] – Ppx: Pyroxene

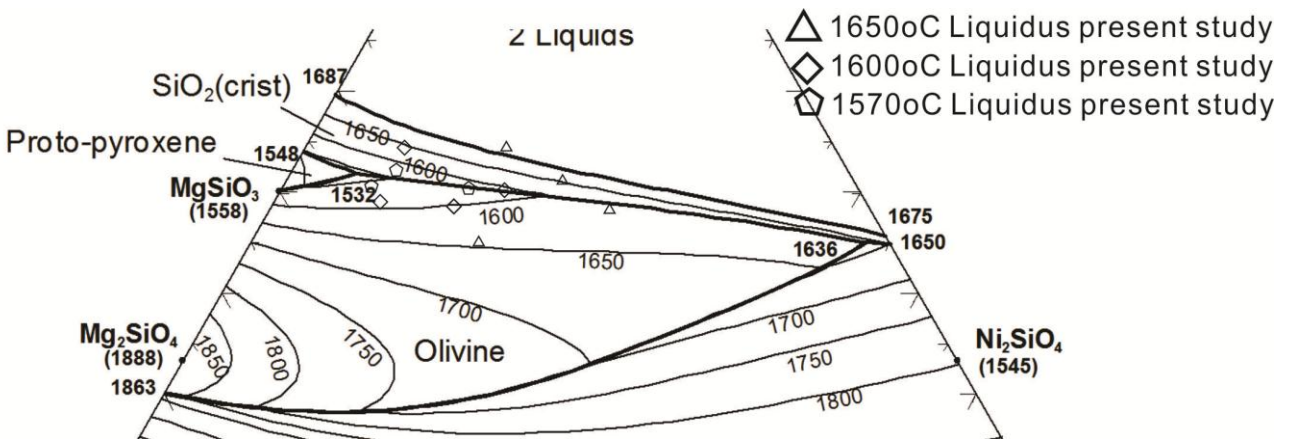
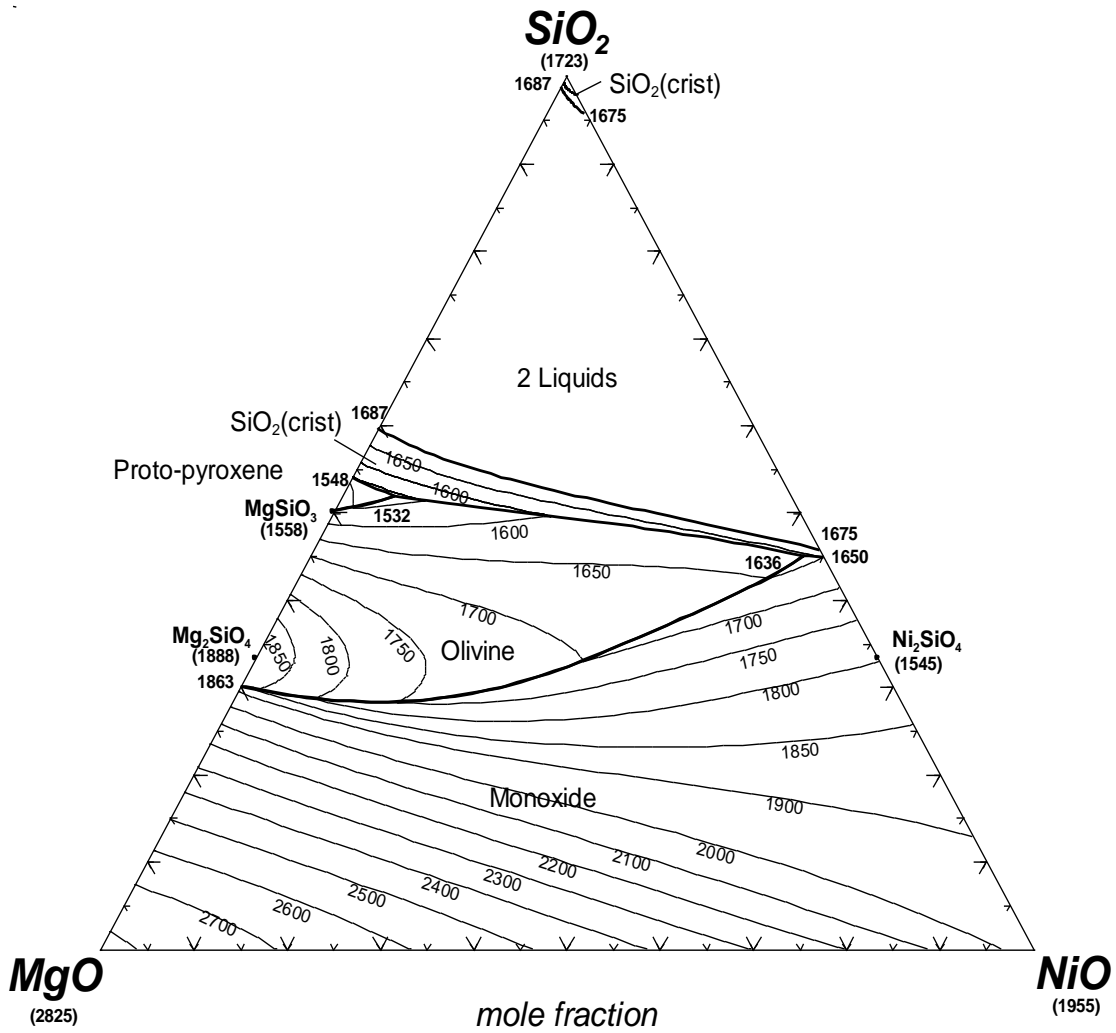


Figure 7 Experimentally determined and calculated liquidus projection of the MgO-NiO-SiO₂ system

In general, the calculated liquidus at 1570, 1600 and 1650 °C is in good agreement with the results of the current study in the olivine primary phase field, as shown in Figure 7. In the cristobalite primary phase field, current experimental results have indicated more dramatic increase of dissolution of SiO₂ in the liquid at 1650 °C compared to the prediction.

4. Conclusion

Integrated research program is under way to develop a thermodynamic database for the Ni laterite smelting process. The recent program incorporates experimental and thermodynamic modelling studies. The NiO-MgO-SiO₂ and NiO-CaO-SiO₂ systems were experimentally investigated and reported and the NiO-CaO-MgO-SiO₂ thermodynamic database was developed as a basis for the Al₂O₃-CaO-FeO-Fe₂O₃-NiO-MgO-SiO₂ system.

The previously available data and new experimental data of the system were critically evaluated and used to obtain a self-consistent set of model parameters for all binary, ternary and higher order sub-systems. The Modified Quasi-chemical model was used to describe the Gibbs free energy as functions of temperature and composition. The models reproduce experimental data within experimental error limits and permit making estimations of the thermodynamic properties of multi-component solutions.

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References

- [1] C.W. Bale, A.D. Pelton and W.T. Thompson: "Facility for the Analysis of Chemical Thermodynamics" (FACT), *Ecole Polytechnique, Montreal, Canada*, 1996
- [2] A.D. Pelton, M. Blander, in: H.A. Fine, D.R. Gaskell (Eds.), *Proceedings of the Second International Symposium on Metallurgical Slags and Fluxes*, 1984, TMS-AIME, Warrendale, PA., p281-294.
- [3] A.D. Pelton, M. Blander. *Metall. Trans. B*, 1986, 17B , p805-815.
- [4] M. Hillert, B. Jansson, B. Sundman, *Z. Metallkd.* 1988, 79 (2), p81-87.
- [5] I.-H. Jung, S.A. Deckerov, A.D. Pelton, *J. Eur. Ceram. Soc.* 2005, 25(4), p313-333.
- [6] G.M. Biggar, *J. Am. Ceram. Soc.* 1969, 52(6), p316-317.
- [7] E.B. Pretorius, A. Muan, *J. Am. Ceram. Soc.* 1992, 75(6), p1458-1462.
- [8] S. Mukhopadhyay, K.T. Jacob, *Metall. Mater. Trans. A*, 1995, 26A (9), p2311-2315.
- [9] F.E. Campbell, P.L. Roeder, *Am. Mineral.* 1968, 53(1-2), 257-268.
- [10] S. Seifert, H.S.C. O'Neill, *Geochim. Cosmochim. Acta*, 1987, 51(1), p97-104.
- [11] S. Mukhopadhyay, K.T. Jacob, J., *Phase Equilib.*, 1995, 16(3), p243-253.
- [12] Y. Shirane, J. Japan *Inst. Metals.*, 1975, 39(9), p908-916.
- [13] G. Ottonello, R. Morlotti, *J. Chem. Thermodyn.* 1987, 19(8), p809-818.
- [14] A.E. Ringwood, *Geochim. Cosmochim. Acta*, 1956, 10(5-6), p297-303.
- [15] M.W. Grutzeck, A. Muan, *J. Am. Ceram. Soc.* 1988, 71(8), p638-643