

HIGH TEMPERATURE PHASE EQUILIBRIA IN NICKEL-CONTAINING OXIDE AND SILICATE SYSTEMS RELEVANT TO FERRO-NICKEL PRODUCTION

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ABSTRACT

A range of technologies are used to recover ferro-nickel from lateritic ore sources. The chemistries of these ores 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 operating temperatures, improve Ni extraction, reduce operating costs and support the development of novel commercial pyrometallurgical extraction processes.

Using new experimental techniques that have been developed for the measurement of high temperature equilibria under controlled conditions important new fundamental information has been obtained characterising the chemical behaviour of key NiO-containing multi-component oxide systems at conditions of interest to nickel pyrometallurgical processes. The research has lead to the development of a new self-consistent, multi-phase, multi-component thermodynamic database that can be used in conjunction with thermochemical software FactSage to predict complex phase equilibria and thermodynamic properties in this system.

Using the newly developed database predictions the effects of composition, temperature and gas composition on the complex phase equilibria present in high temperature process conditions relevant to Fe-Ni processing and smelting can be provided.

KEYWORDS: Oxides, slags, alloy, phase equilibria, thermodynamic modelling, ferro-nickel.

1. INTRODUCTION

The production of nickel from Ni Laterite ores containing both Limonite (mainly Fe hydroxide) 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. The research 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

Advanced experimental procedures for phase equilibrium measurements have been developed by the PYROSEARCH at the University of Queensland [1]. The technique involves high temperature equilibration of a synthetic oxide sample in a controlled gas atmosphere. The sample is then rapidly quenched so that the phase assemblage present at high temperature remains unaltered. The quenched sample is mounted in epoxy resin, polished for metallographic examination and microanalysis, and the compositions of the crystalline solid phases are measured by electron probe X-ray microanalysis (EPMA) with wavelength dispersive detectors (WDD).

2.2.1. 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), SiO₂ (99.98 wt% purity) and Ni (99.8 wt% purity) powders 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 at least 2 condensed phases are present at equilibrium. 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 Matthey (Melbourne, Australia) were used as sample containers. Special care was taken to minimize the contact area between the sample and the Pt-envelopes, before equilibration, to minimize contamination from Pt.

2.2.2. 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) heating 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 in a controlled gas atmosphere for more than 30 minutes, and the specimen was then raised into the uniform temperature hot zone of the furnace.

2.2.3. 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.

2.2.4. Sample preparation for analysis

After the equilibration, the specimen was rapidly quenched by dropping it directly into the iced water so that the phases present at high temperature and their compositions are retained at room temperature. The quenched sample was dried on a hot plate at about 100°C, fractured into

smaller pieces, which were mounted in epoxy resin, polished using conventional metallographic polishing techniques and carbon coated for subsequent electron probe X-ray micro-analysis (EPMA).

2.2.5. Microstructure imaging

The microstructures of polished samples were examined using optical microscopy, and then Scanning Electron Microscopy (SEM). Images shown in present study are backscattered electron images in which phases are distinguished by difference in average atomic weight.

2.2.6. Analysis technique

The rapid quenching technique successfully retains phase assemblages and phase compositions present at equilibration temperatures so that they can be subsequently measured at room temperature. 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 (CaSiO_3) for Ca and Si, magnesite (MgO) for Mg and Ni olivine (Ni_2SiO_4) 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 1wt%. EPMA is used to measure the total metal cation concentrations; no information on the proportions of the same element having different oxidation states can be usually acquired by direct measurement, all metal concentrations are recalculated to selected oxidation state for convenience of presentation and to unambiguously report the compositions of the phases.

Many earlier phase equilibria studies were carried out using high-temperature equilibration and quenching techniques followed by XRD analysis for phase identification and for the determination of phase boundaries. For sub-solidus phase equilibria studies, there are several advantages of the EPMA over the XRD technique; these include the following.

- Increased accuracy: EPMA, including the measurement of phase composition, is carried out after the equilibration experiment, avoiding uncertainty due to the unavoidable loss of components or materials during the sample preparation and equilibration process, i.e., loss through vapour phase reactions or reactions with containment materials.
- Microanalysis capability: The quantitative analysis of the composition of the phases can be carried out accurately in a small area 1 to 2 μm in lateral size, which can be used for evaluating local equilibrium.
- Imaging capability: The secondary and backscattered electron imaging provide additional information for evaluating the phases present and their morphology, and for evaluating other microstructural characteristics.
- The EPMA technique, can detect and measure to small variations in the concentrations of metal cations and accurately determine the phase boundaries and solid solutions, XRD on the other hand cannot detect phase present at low concentrations.

2.2.7. Assessment of achievement of equilibrium

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

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. All samples were thoroughly examined to ensure the phases in the final results correspond to the equilibrium.

2.3. Thermodynamic modeling

The thermodynamic modelling has been carried out using the FactSage thermochemical software and its databases [2]. 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 [3-4] in which short-range-ordering is taken into account. Solid solutions are mainly modelled in the framework of the Compound Energy Formalism [5], taking into account the crystal structure and physical nature of each solution. Some other solution phases were optimized earlier [6]. 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 formulae and notations are all given in table 1. Cations shown within a set of parentheses occupy the same sublattice.

3. RESULTS AND DISCUSSION

3.1. CaO-NiO-SiO₂

Phase equilibria in the CaO-NiO-SiO₂ system were studied by several authors [7-9] 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 [7] and Pretorius and Muan [8] 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 [7]. Biggar [7] 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 [7] were considered questionable since it was rather difficult to describe them in subsequent thermodynamic optimization. To resolve this issue, the CaO-NiO-SiO₂ ternary phase equilibria have been

experimentally investigated.

Table 1: 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
Hatrurite	Ca ₃ SiO ₅	
Rankinite	Ca ₃ Si ₂ O ₇	
Silica (quartz, tridymite, cristobalite)	SiO ₂	qz, trid, crist

Examples of typical microstructures of equilibrated samples are shown in figure 1. The equilibrated phases were found to have good contact with each other and a dense microstructure 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.

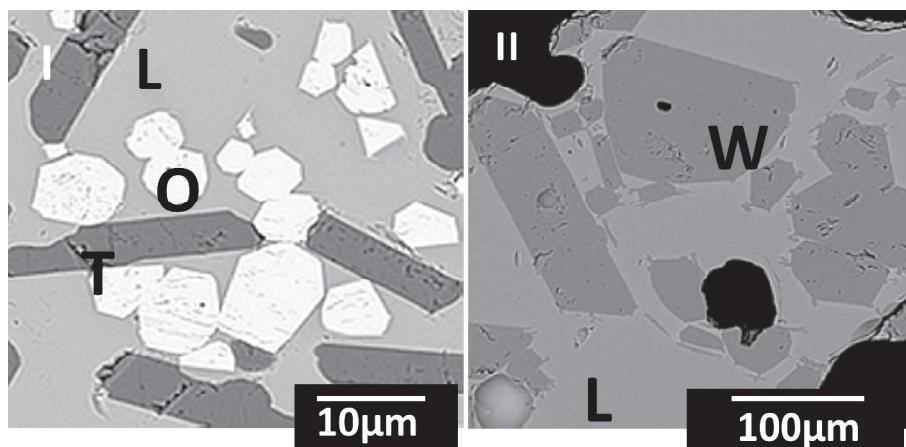


Figure 1: Backscattered SEM micrographs typical of equilibrated Ni-Ca-Si-O systems
I) Liquid (L), Olivine (O) and Tridymite (T) at 1643.15 K in air;
II) Liquid (L) and wollastonite (W) at 1673.15 K in air

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 to be 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 [7] were erroneous, therefore, they were not taken into

consideration during optimisation; experimental results in the liquid- CaSiO_3 region were found to be well described using the revised model within experimental error limit; however, less SiO_2 in the liquid in the liquid- SiO_2 - CaSiO_3 region at 1360 °C was predicted using the databases developed in present study.

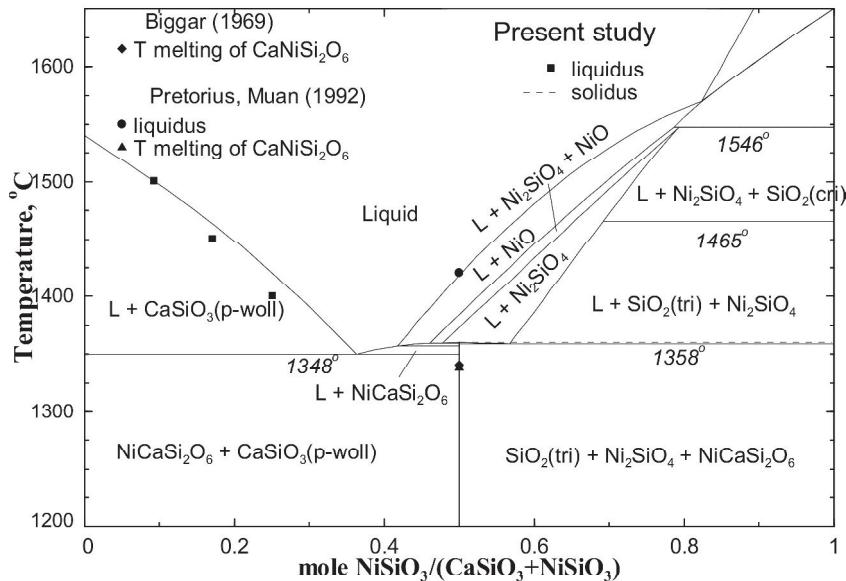


Figure 2: Calculated CaSiO_3 - NiSiO_3 section of the CaO - NiO - SiO_2 system along with the literature data [7-8] and results from the current experiments

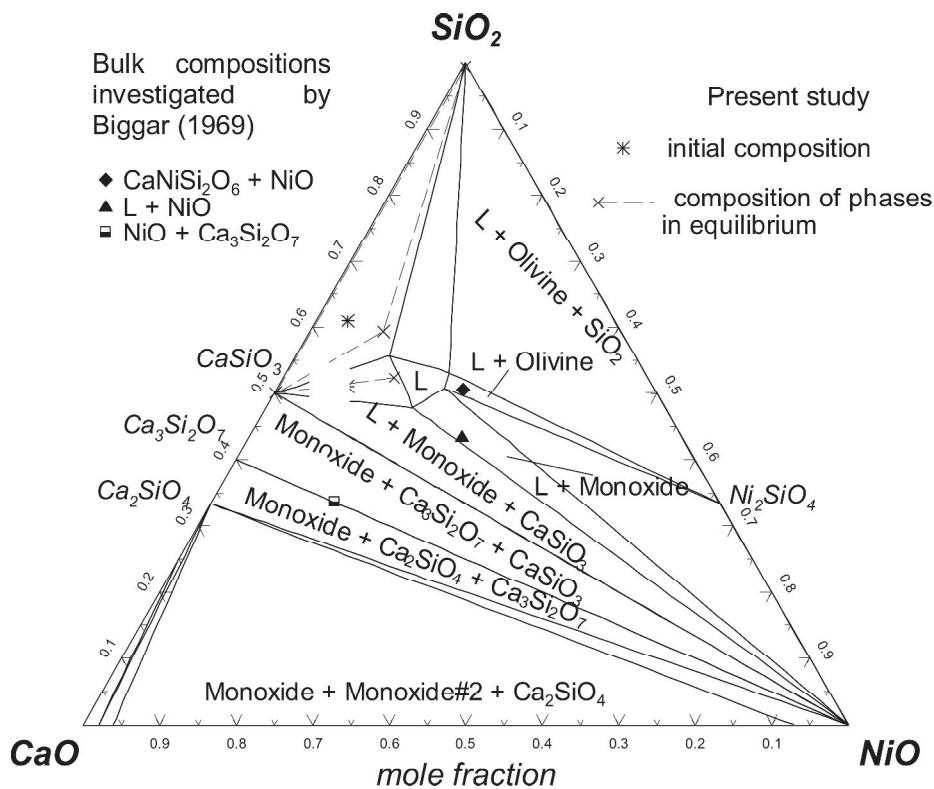


Figure 3: Calculated isothermal section of the CaO - NiO - SiO_2 system at 1360°C along with the literature data of Biggar [7] and experimental results from the present study

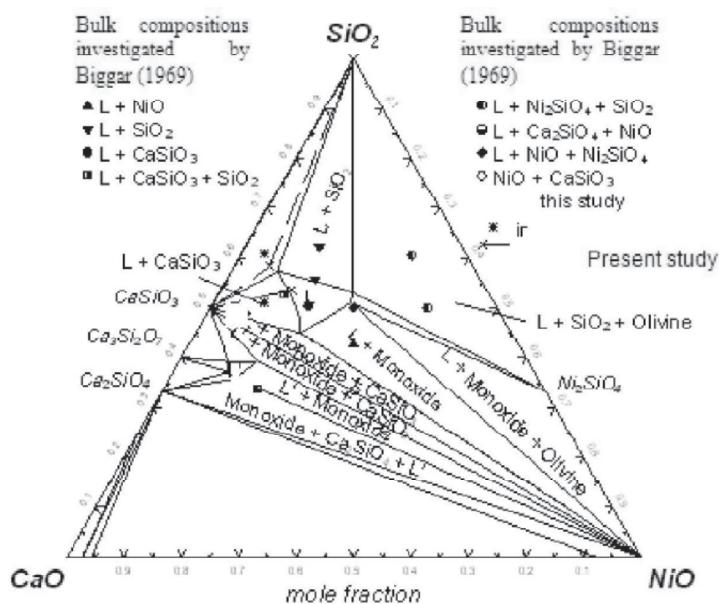


Figure 4: Calculated isothermal section of the CaO-NiO-SiO₂ system at 1390°C along with the literature data of Biggar [7] and experimental results for the present study

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 [10-13]. 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 [14] indicate that there is not 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.

Limited Phase equilibria data including the liquid phase are available and some inconsistencies were found in the published literature. Ringwood [15] determined the phase diagram of the orthosilicate Mg₂SiO₄-Ni₂SiO₄ section using quenching technique followed by an optical microscopic observation, the data obtained 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 [16] measured phase equilibria in the MgO-NiO-SiO₂ system by employing a 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.

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.

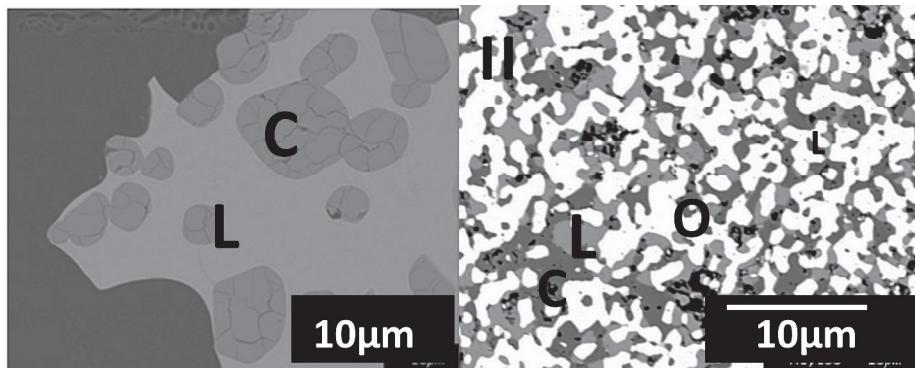


Figure 5: Backscattered SEM micrographs typical of equilibrated Ni-Mg-Si-O systems
(I) Liquid (L) and Cristobalite (C) at 1643.15 K in air
(II) Liquid (L), Olivine (O) and Cristobalite (C) at 1673.15 K in air

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 cristabolite primary phase field, current experimental results have indicated more dramatic increase of dissolution of SiO_2 in the liquid at 1650°C compared to the prediction.

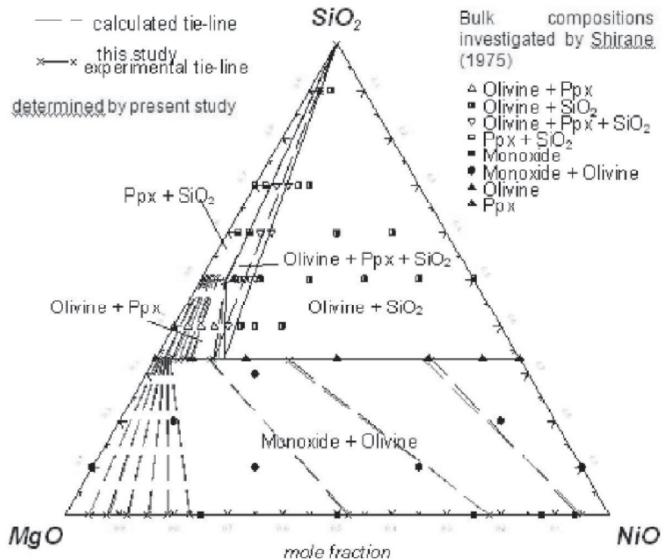


Figure 6: Isothermal section of the $\text{MgO}-\text{NiO}-\text{SiO}_2$ system at 1400°C along with the calculated and experimental tie-lines measured in this study, and previously reported experimental results [10,13] –Ppx: Pyroxene

4. CONCLUSION

An integrated research program is under way to develop a new 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.

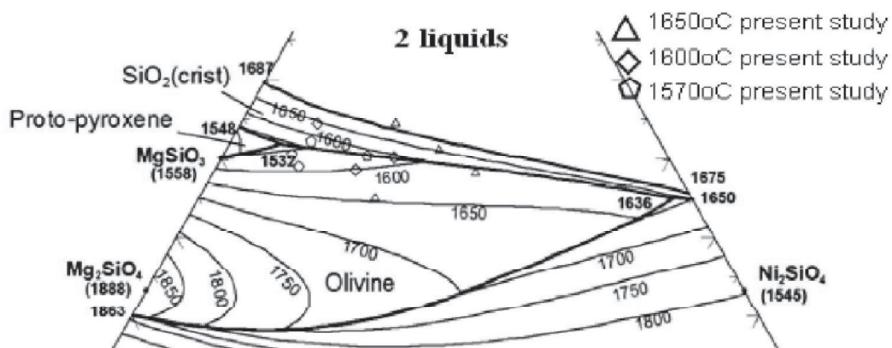


Figure 7: Experimentally determined and calculated liquidus projection of the MgO-NiO-SiO₂ system

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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