Experimental and thermodynamic study of the phase equilibria in the NiO-CaO-FeO-Fe_2O_3 system in air and in equilibrium with metal (Fe-Ni) alloy

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ABSTRACT

This study represents a part of comprehensive research aimed at integrating nickel into a thermodynamic database constantly developed at Pyrosearch. The behaviour of Ni in calcium-ferrite slags is considered. An integrated approach combining experimental and thermodynamic modelling methods has been employed to predict phase equilibria in the NiO-CaO-FeO-Fe_2O_3 system under oxidizing conditions and in equilibrium with the metal FeNi phase.

The compositions of liquid slags and coexisting solid solutions have been determined through the analysis of equilibrated and quenched samples by electron probe microanalysis technique (EPMA). The research results are presented in the form of liquidus projections on the corresponding phase diagrams, considering both oxidising and reducing conditions. The solubility of Ni in spinel, dicalcium ferrite and calcium oxide as well as solubility of Fe and Ca in Ni monoxide, have been examined under several atmospheric conditions. Additionally, the compositions of the NiO-FeO monoxide in equilibrium with metal phase have been studied. The experimental data not only support the outcomes of thermodynamic modelling but also validate the parameters of the applied thermodynamic models, thus confirming the reliability and accuracy of the integrated approach.

INTRODUCTION

A comprehensive experimental and thermodynamic study of high-temperature phase equilibria in multicomponent systems, relevant to materials and products of non-ferrous metallurgy, is crucial for prediction, managing and optimisation industrial processes. Many applied studies rely on accurate thermodynamic descriptions. Therefore, fundamental studies of phase equilibria, supplemented by thermodynamic optimisation make the essential tools for metallurgists worldwide.

The multicomponent NiO-CaO-FeO-Fe_2O_3 system falls within a range of basic oxide systems that are related to Ni-containing slags of nonferrous metallurgy. Compounds of this system are present in slags formed during the recovery of Ni and other metals from WEEE (Waste electrical and electronic equipment) (Bigum et al., 2012; Coman et al., 2013). Under reducing conditions, when the slag phase reaches equilibrium with FeNi metal, it becomes relevant to Caron the process, widely utilised for treatment of nickel laterite ores (Rhamdani et al., 2009; Meshram et al., 2019). Optimizing the slag composition is critical for achieving high nickel recovery rates, minimizing energy consumption, and reducing environmental impacts associated with nickel production. Thus, a thorough understanding of phase equilibria in the NiO-CaO-FeO-Fe_2O_3 system enables researchers to tailor slag composition to enhance nickel recovery efficiency and overall process performance in both primary and secondary metallurgy.

Phase equilibria in boundary CaO-FeO-Fe_2O_3 system in air has been initially investigated by Philips and Muan (Philips and Muan, 1958), followed by Schurmann and Kraume (Schurmann and Kraume, 1976), laying the foundation for the thermodynamic description of the system. In 2016 this system has been optimised by Hidayat (Hidayat et al., 2016), and further experimentally revised by Cheng (Cheng et.al. 2021). The CaO-FeO system in equilibrium with Fe metal has also been extensively studied (Hidayat et al., 2016). While the NiO-FeO-Fe_2O_3 system has been studied by less extent, some thermodynamic and calculated data have been published in Prostakova's thesis (Prostakova, 2013). However, there remains a lack of experimental data on phase equilibria in the high-temperature region close to the liquidus surface of the system. Regarding the studied quaternary NiO-CaO-FeO-Fe_2O_3 system, only two experimental papers have focused on measuring the solubility of CaO in FeNi spinel at 1200°C (Yamamura et al., 1981) and at 1300°C (Vasiliu, 1979). The calculated isothermal sections of the system at 1200 and 1300°C have been plotted in Prostakova's thesis (Prostakova, 2013), but these data have not been supplemented by accurate experimental results.

Therefore, the aim of the present study is to define phase equilibria in the NiO-CaO-FeO-Fe_2O_3 system at high-temperatures in air and in equilibrium with the metal phase. The study will cover aspects such as defining the solubility of CaO in spinel and Ni monoxide solutions, defining the solubility of Ni in lime and dicalcium ferrite solutions and revising the positions of monovariant lines and locations of invariant points. In equilibrium with the metal phase, the temperature of the experiments will be limited by formation of liquid FeNi alloy (approximately 1450 °C), and the operating partial pressure will range from $10^{-5.5}$ to 10^{-9} atm.

EXPERIMENTAL STUDY

The experimental methodology employed in this study involves high temperature equilibration under controlled conditions, rapid cooling (quenching) and direct measurement of the phase compositions using electron probe X-ray microanalysis (EPMA) (Jak et al., 1995; Jak et al., 2012).

The obtain the desired phase assemblages, NiO, FeO, Fe_2O_3, CaO powder oxides, as well as Fe and Ni metals have been utilised in the mixtures. All reagents were sourced from Alfa Aesar company (MA, USA) and characterised with a purity of 99.9 wt. % and higher. To simulate the composition of dicalcium ferrite a master slag with a CaO: FeO mass ratio of 1:1 was preliminary prepared. The proportions of reagents in the initial mixtures were determined through calculations using FactSage and a current version of confidential thermodynamic database to produce one or two solid crystalline phases (Ni monoxide, lime, spinel or dicalcium ferrite) in equilibrium with liquid slag and FeNi metal (for the second case). Prepared mixtures were pressed into 0.2-0.3 gram pellets prior to equilibration.

Preliminary prepared substrates from high purity Fe_3O_4 (spinel), NiO (Ni monoxide), $Ca_2Fe_2O_5$ (dicalcium ferrite) and SiO_2 (tridymite) were used to support the mixtures for equilibration in air. Ni folded baskets were employed as substrates for equilibration in the presence of the FeNi phase. The overall illustration of the different types of substrates as well as details of substrates preparations are published by Sineva et al. (Sineva et al., 2023). The idea was to apply substrates made of primary crystallised phase depending on the bulk composition of the initial sample.

To study samples in an air atmosphere, compressed air with a total flow of 500 ml/min has been passed through the furnace. For the system in equilibrium with FeNi phase over a range of $p(O_2)_{s,}$ the oxygen partial pressure was controlled using mixtures of $Ar/CO/CO_2$ at different ratios depending on the target of $p(O_2)$ value. Furnaces temperatures ranged from 1200 to 1600 °C for experiments in air and from the 1250 to 1450 °C for those in equilibrium with the metal phase. Temperature measurements were verified using a Pt/PtRh10% thermocouple adjacent to the experimental sample and calibrated against a standard thermocouple supplied by the National Measurement Institute of Australia (NSW, Australia). The equilibration time was 6 hours, determined through preliminary experiments. Following equilibration, samples were rapidly quenched into a 20% $CaCl_2$ -H_2O solution maintained at -20 °C. Subsequently, samples were thoroughly washed in water end ethanol, dried, and mounted in epoxy resin for further polishing using conventional metallographic techniques.

A JEOL JXA8200L (trademark of Japan Electron Optics Ltd., Tokyo) electron probe X-ray microanalyser (EPMA) with wavelength dispersive detectors (WDD) was used to get the images of the microstructures of the experimental samples and to measure the concentrations of the elements in different phases. The EPMA was employed at an acceleration voltage of 15 kV and a probe current of 20 nA. Pure Fe_2O_3, $CaSiO_3$,SiO_2 and $NiSiO_3$ reference standards were used to measure the composition of the slags and solid oxides phases. Fe and Ni metals served as standards for measurement metal phases composition. All referenced materials were provided by Charles M.Taylor. The concentrations of the components in slag and solid oxide phases were recalculated to selected oxidation states for presentation convenience and to unambiguously report the compositions of the phases, while Fe was expressed as FeO for experiments in equilibrium with metal phase and as Fe_2O_3 for experiments in air.

RESULTS AND DISCUSSIONS

I. NiO-CaO-FeO-Fe_2O_3 system in air

The typical microstructures illustrating phase compositions of the experimental samples are given in Fig. 1. In each microstructure, the liquid slag exists in equilibrium with one or two solid phases, which represents spinel, Ni monoxide, dicalcium ferrite, or lime solutions. The compositions of all phases have been determined using EPMA, recalculated to mol.% and then plotted on calculated version of liquidus surface of the NiO-CaO-$FeO_{1.5}$ system. The resulting phase diagram is illustrated in Fig. 2. Compositions of the liquid slags in equilibrium are denoted by red circles, tie-lines are represented by blue dashed lines, connect to compositions of the corresponding solid phases. The calculated version of the phase diagram has been generated using the Equilib module of FactSage 7.3 software, utilising the most recent version of a confidential thermodynamic database. In is shown, that the compositions of the lime, spinel, Ni monoxide and dicalcium silicate (C_2F) solid solutions are predicted quite accurate with the current version of the database. Experimental validation confirms the solubility of Ni in lime, spinel, and C_2F solutions. However, slight deviations are observed between the experimental compositions of invariant points on the liquidus surface and the calculated version. Consequently, it is necessary to reoptimize the temperatures of the invariant reactions based on the acquired experimental data.

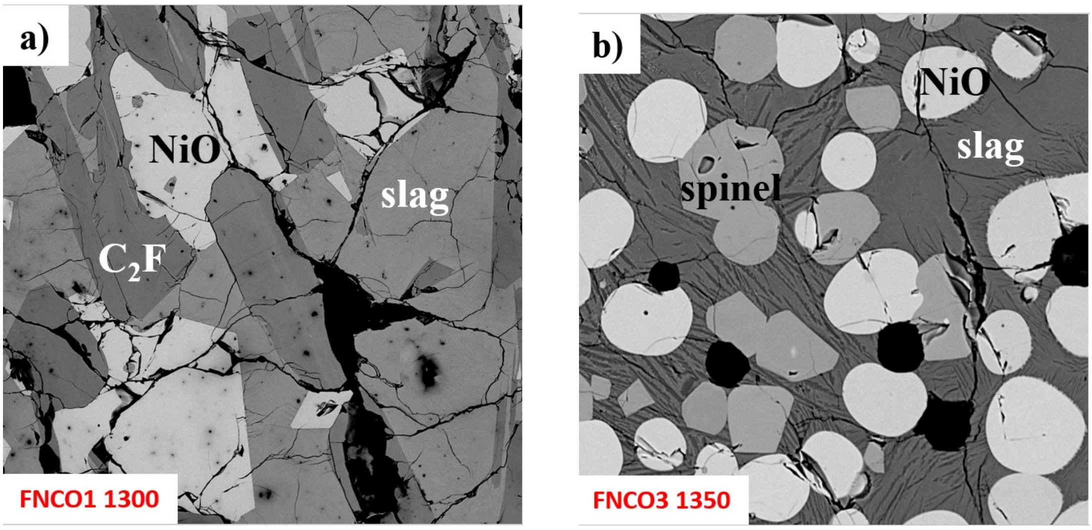

FIG 1 – Back-scattered electron images of the quenched samples, illustrating phase equilibria in the NiO-CaO-$FeO_{1.5}$ system in air at given temperatures a) slag/NiO/ C_2F at 1300 ºC; b) slag/NiO/spinel at 1350 ºC

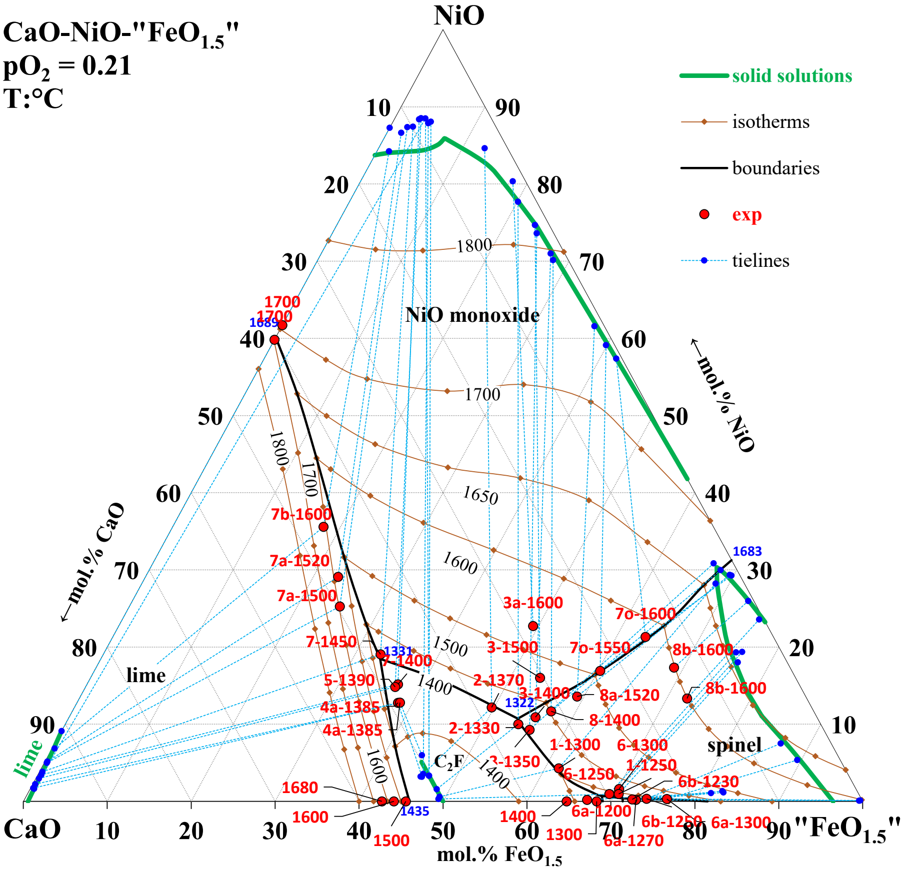

FIG 2 – Phase diagram of the NiO-CaO-$FeO_{1.5}$ system in air

As it was mentioned before, all solid phases are characterised by homogeneity ranges. Fig. 3 illustrates compositions of the solid phases in the NiO-CaO-$FeO_{1.5}$ system in air as functions of slag composition and temperature. Majority of the experimental points are located on the boundary lines between phases because most of the experimental slag is in equilibrium with two crystalline phases and located on monovariant line. It is shown that temperature trends, based on experimental points are in quite good agreement with calculated data.

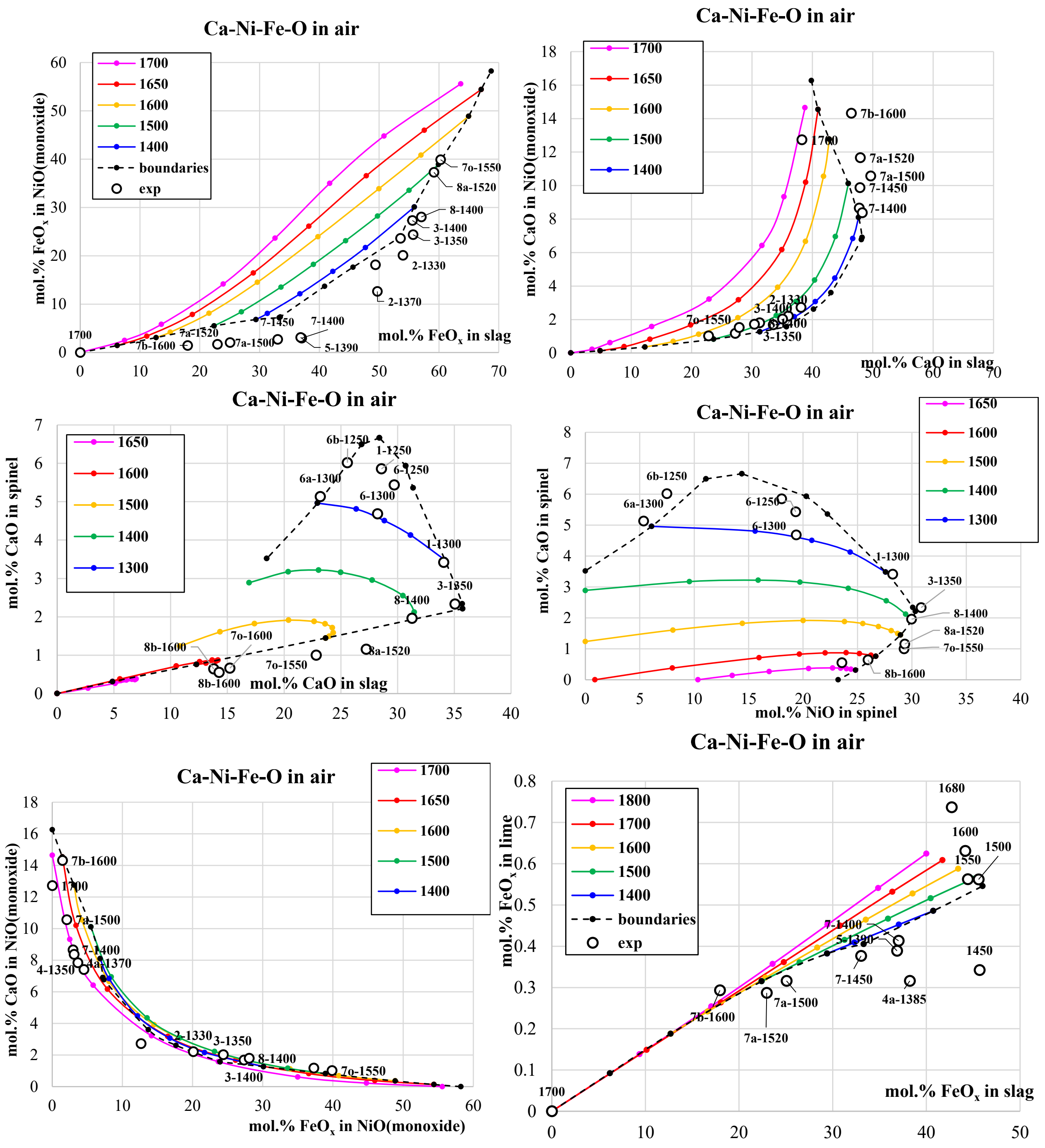

FIG. 3- Compositions of the solid phasess : (a,b, e) NiO monoxide; (c,d) spinel and (f) lime in the the NiO-CaO-FeO$_x$ system in air as functions of slag or solid phases compositions and temperature (ºC). Lines and boundaries of all solid solutions are calculated with current version of confidential thermodynamic database, points are experimental data of the study.

Obtained experimental data allow to include Ni in the thermodynamic models for better description of lime and dicalcium ferrite solutions, as well as include Ca in Ni monoxide and Ni spinel phases.

II. NiO-CaO-FeOx system in equilibrium with metal FeNi phase

Fig. 4 illustrates high-temperatures slag/FeNi metal/solid solution (lime, Ni monoxide or C$_2$F) phase equilibria. Due to fix both parameters at the same time (oxygen partial pressure and temperature) it's unable to get equilibrium of slag and metal with two solid phases (the system would be over fixed in that case). Therefore, all the points of liquid slags are located in the fields of primary phases crystallisations, but not on monovariant lines. Calculated small phase area of spinel and CWF (CaO*FeO) solutions existed in low temperatures area (below 1250 °C) have not defined experimentally.

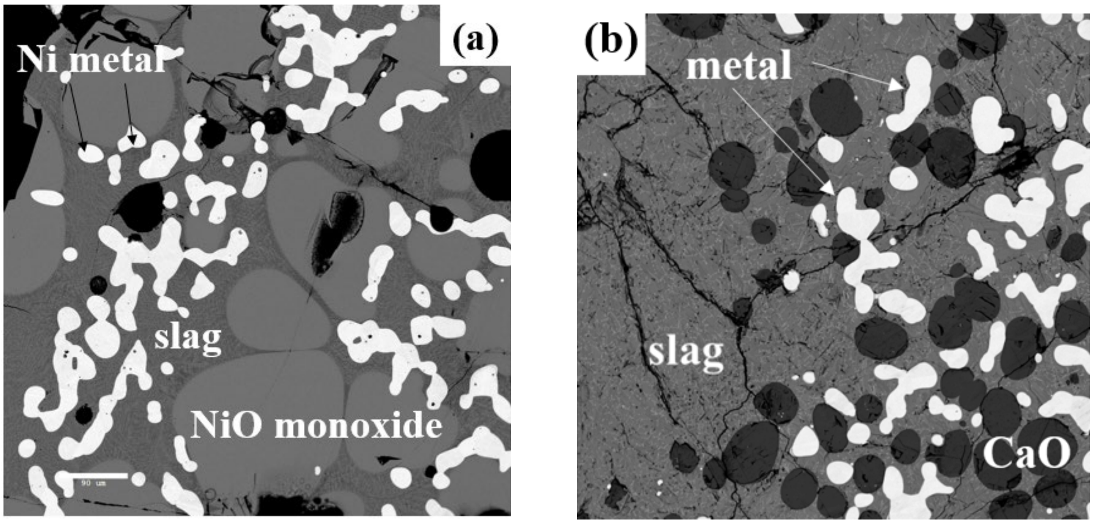

FIG. 4- Back-scattered electron images of the quenched samples, illustrating phase equilibria in the NiO-CaO-FeO1.5 system in equilibrium with metal phase at given temperatures a) slag/NiO monoxide/metal at 1500 ºC; b) slag/CaO/metal at 1400 ºC

Obtained experimental data have been plotted on calculated version of the liquidus projection of the NiO-CaO –FeOx system. The resulting phase diagram is illustrated in Fig. 5(a). The zoomed area of phase diagram with low NiO concentration is illustrated in Fig 5(b) for better representation of small phase areas as well as compositions of lime, C_2F and monoxide solutions. Compositions of the liquid slags in equilibrium with other phases are identified by red circles, tie-lines are blue dashed lines ending with compositions of corresponding solid phases. Calculated version of the phase diagram calculated in Equilib module of FactSage 7.3 software with employing of current version of confidential thermodynamic database.

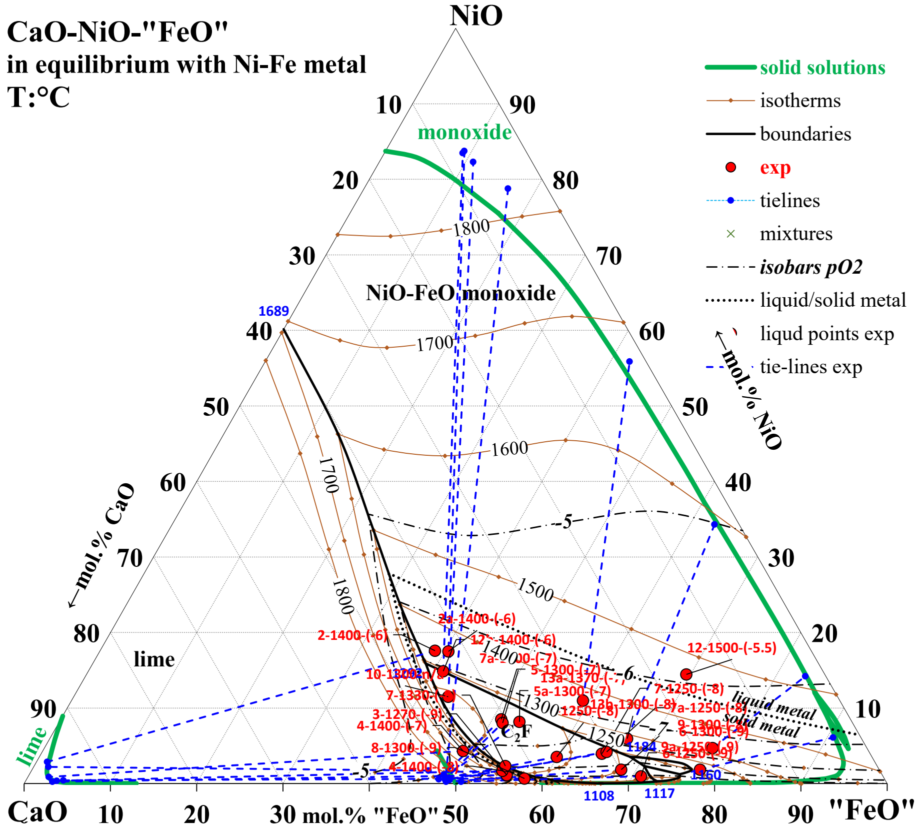

FIG.5(a) - Phase diagram of the NiO-CaO-FeO_x system in equilibrium with metal Fe-Ni phase

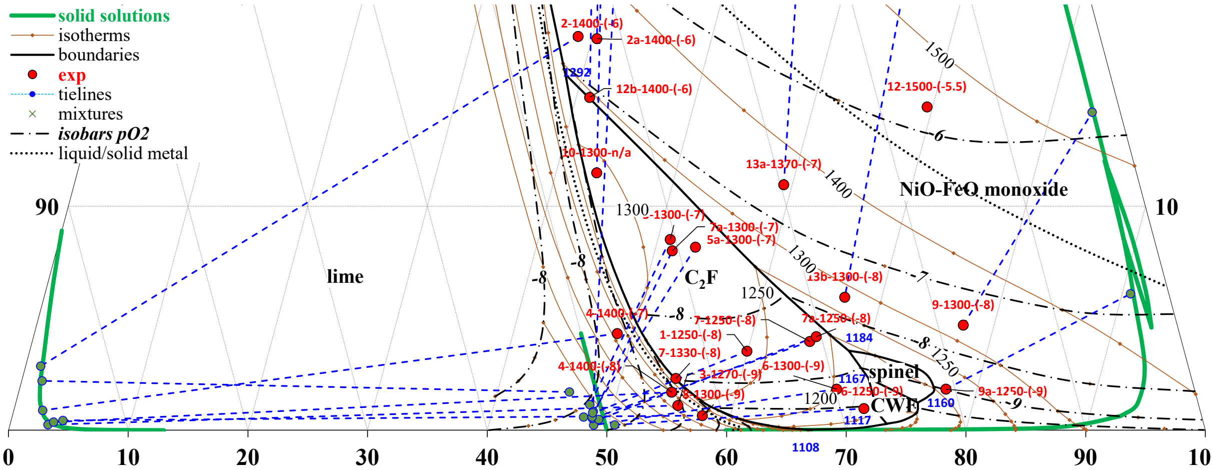

FIG. 5(b)- Zoomed area with low NiO concentration of the phase diagram of the NiO-CaO-FeO$_x$ system in equilibrium with metal phase

Based on the experimentally defined slag compositions the isotherms and isobars within the studied system will be corrected. A good agreement is observed between calculated and experimental compositions of lime, C_2F and NiO-FeO monoxide solutions. The only exception is dissolution of CaO in monoxide solution in high NiO-containing area.

Measured compositions of the slag, metal, and solid phases as functions of $P(O_2)$ and Ni concentration in slag have been plotted in Fig.6

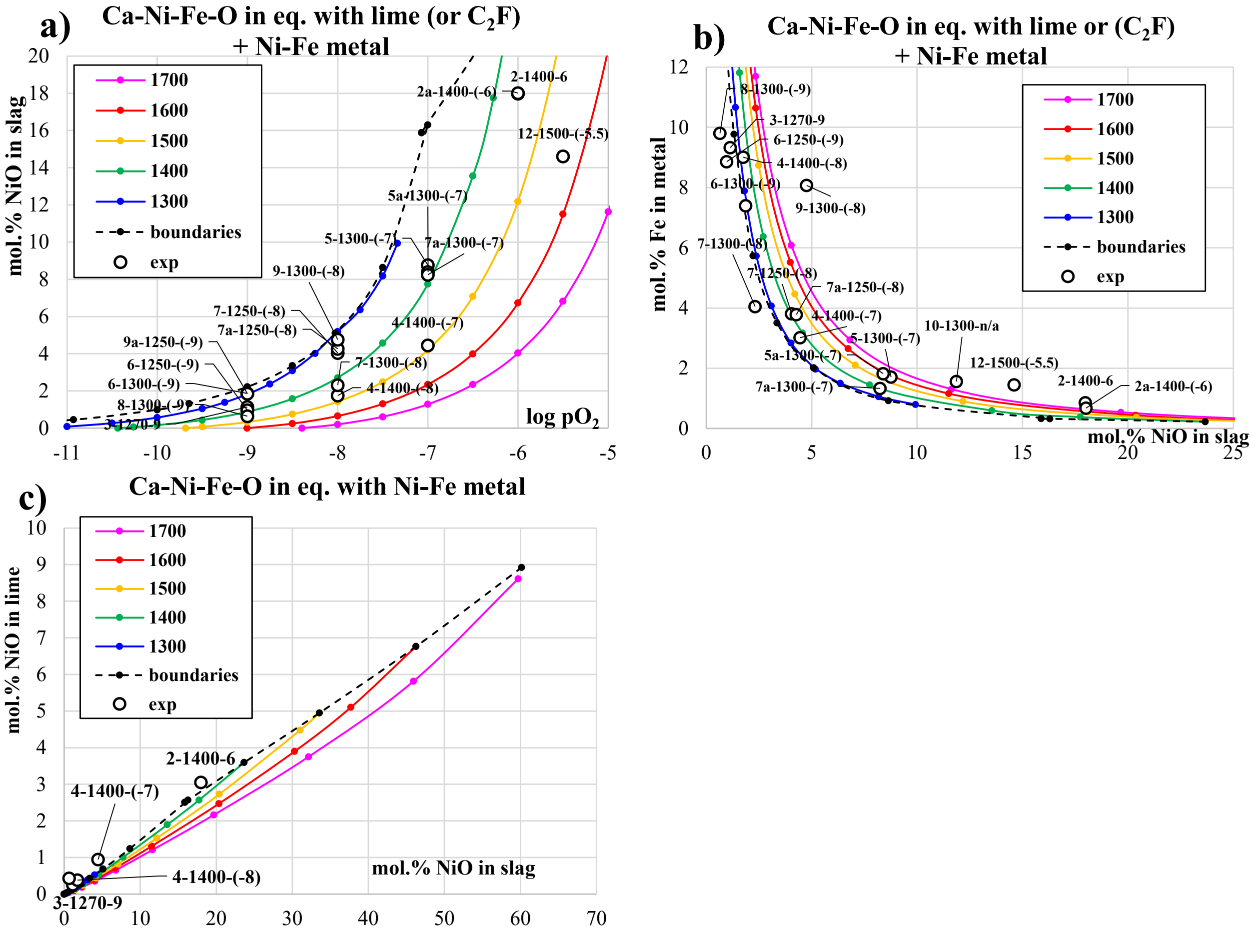

FIG. 6- Compositions of phases (a) slag; (b) metal and (c) lime phases in mo.% in the the NiO-CaO-FeO$_x$ system in equilibrium with metal phase as functions of slag composition, $P(O_2)$ (atm) and temperature (°C). Lines for all solid solutions are calculated with current version of the UQPY (beta-version) database

CONCLUSIONS

Phase equilibria in the high-temperature region of the NiO-CaO-FeO-Fe_2O_3 system in air and in equilibrium with the metal phase have been studied using the integrated approach, which combines thermodynamic predictions with the "equilibration-quenching-EPMA" experimental technique. The resulted liquidus surfaces of the NiO-CaO-Fe_2O_3 system and NiO-CaO-FeO/FeNi system have been plotted. Particular emphasis has been placed on defining the homogeneity ranges of lime, dicalcium ferrite, NiO-FeO monoxide and spinel solutions. The solubility of Ni in lime and C_2F solutions has been precisely characterised and validated through experimental data. The solubility of CaO in spinel and NiO-FeO monoxide solutions has been determined. When in equilibrium with metal phase the concentration of Ni in slag as a function of oxygen partial pressure has been defined experimentally.

This study has been performed as a part of integrated research program, aimed at complete characterization of the gas-slag-matte-speiss-metal-solids equilibria in the Cu-Pb-Zn-Fe-O-S-SiO_2-(Al_2O_3-CaO-MgO-Cr_2O_3)-(As-Sn-Sb-Bi-Sn-Au-Ni-Co) system.

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